Quantum mechanics and spectroscopy:
Another workbook

M. Kuno

January 29, 2006

Contents

1 Preface 1

2 Revision History 3

3 Introduction 5

4 Fundamentals 15

5 Schrödinger Equation 35

6 Particle in a 1D Infinite Box 39

7 Particle in a 1D Symmetric Box 43

8 Alternative particle in a box problems 47

9 Particle in an infinite 3D box 53

10 Particle in a sphere 61

11 Harmonic Oscillator: Analytical approach 69

12 Harmonic Oscillator: raising and lowering operators 77

13 Rigid Rotor 89

14 Selection Rules 97

15 Potential Step 101

16 Potential Barrier 105

17 Nondegenerate perturbation theory **115**

18 Degenerate perturbation theory **129**

19 The WKB Approximation **151**

20 Time dependent perturbation theory **157**

21 Rabi Solutions, Schrodinger Representation **171**

22 Multilevel absorption, Schrodinger Representation **179**

23 Rates, Schrodinger Representation **185**

24 2nd order time dependent perturbation theory **193**

25 Three pictures of quantum mechanics **199**

26 The interaction representation **203**

27 Two level system revisited **211**

28 1st order transitions, Interaction representation **219**

29 Adiabatic perturbations **229**

30 Fermi's Golden Rule **235**

31 Fermi's First Golden Rule **239**

32 Line Broadening (lifetime broadening) **245**

33 Irreversible decay, Fourier transform approach **249**

34 Irreversible decay, Redux **263**

35 Maxwell's equations (and units) **269**

36 Maxwell's equations (Electric and Magnetic Fields) **271**

37 Maxwell's equations ver. 2.0 (More general) **281**

38 Hamiltonian derived from the Lorentz Force **287**

39 Interlude 295

40 The electric dipole approximation and A_0 301

41 More electric dipole stuff 305

42 Second quantization 315

43 Coupling of radiation to matter 325

44 Alternative coupling of radiation to matter 331

45 Emission 337

46 Relation to Einstein Coefficients 353

Chapter 1

Preface

Preface

This is the second packet of lecture notes that I have typeset using LaTex. The basic idea here is the preserve my paper and pencil notes in a more accessible manner that both the students and I can retain. Although my memory on when these notes were put together has begun to slip I believe I worked on them towards the end of the summer of 2004. I also recall typing these notes in the hotel at the fall ACS meeting held in Philadelphia that year. The text might appear to be a little forced together given the short first semester quantum section that I have at the beginning. This is because there was a last minute change to the teaching assignment and I basically taught quantum that year even though I was supposed to do spectroscopy. My spectroscopy notes are now being typeset into LaTex and should be up shortly as a separate packet. A good chuck of the later time dependent part of these notes comes from handwritten notes I took over 10 years ago when I took such a class from Keith Nelson at MIT. The class was 5.74 and I have fond memories of sitting in some classroom on the first floor of building 2 (yes, the same one as in the movie Good Will Hunting) that might have come straight out of the 1920s. There was also some massive wavepacket simulation we were supposed to do for the class and I also remember doing a few all nighters in the basement Athena cluster in building 4. Anyway, the hope is that the next time I teach this class, I can focus more on developing stronger problem sets.

In the future, I will try to add an index when I have a lot of free time. Helps find things. I will also go back and check the sign of $E = \omega A_o$ in the Coulomb gauge, Lorentz gauge section.

M. Kuno 1/29/06

Chapter 2

Revision History

- Version 1 inception, September 25, 2004
- Corrected general typos, 1/06
- Corrected logic bomb in the transmission coefficient section, 1/06
- Corrected logic bomb in the Maxwell, Coulomb and Lorentz gauge section, 1/06
- Added this revision history page, 1/06
- Added the preface, 1/06

Chapter 3

Introduction

Historical stuff

- Towards the end of the 19th century many physicists felt that all the principles of physics had been discovered and that little remained but to clean up and improve the precision of measurments.
- Things looked so good that Michelson of Michelson inteferometer fame (Nobel Prize winner) said in 1894 when opening his lab at the University of Chicago that "future discoveries must be looked for in the 6th decimal place."
- There was great reason to believe this. You had Newtonian mechanics that was well developed which described he behavior of particles through its mass, momentum and velocity, to tremendous accuracy.
- A lot was understood about waves as well. Waves were and still are characterized by an amplitude and frequency. They also exhibit characteristic interference and diffraction phenomena.
- So you had particles on one hand and you had waves on another hand. You could describe pretty much anything as either a particle or as a wave.
- Now one sticking point appeared to be light. There had been a debate going on for a while whether light was a wave or was a particle. This particle viewpoint is referred to as the corpuscular theory of light.
- Newton throught light was a particle. Huygens on the other hand though it was a wave.

- So this debate went on and on for a long time until Young did his famous double slit experiment and basically showed that light exhibited inteference phenomena. This was remarkable because as mentioned above inteference is characteristic of waves. Ok, so now this experiment was thought to have resolved the debate between Newton and Huygens. Light was a wave and Huygens was right.

- The Young double slit experiment basically consists of a light source and a screen with two slits cut into it. The slits are separated by a distance d. Further back is another screen where light from the two slights shines upon. Young noticed that when $n\lambda = dsin(\theta)$ where n is an integer and λ is the wavelength of light you get constructive inteference. So the first inteference maxmium arises at $n = 1$ or when $\lambda = dsin(\theta)$. As mentioned previously, this inteference behavior is characteristic of waves and in turn was thought to solve the debate over the particle or wave nature of light.

- Maxwell then came along and pretty much closed the book on any further debate. His prediction of the electromagnetic nature of light unified the fields of optics, electricity and magnetism. Again, the view that light was a wave came out winning.

- So now all was well in physics. But there were some problems beginning to show even as people were basically congratulating themselves.

- There were a handful of experiments that were a bit of a mystery and could not be properly explained by “classical” physics. What were these experiments? There were four (or five) of them at least of which I’ll describe three.

- **Blackbody radiation**; (solved by Planck)

- **The photoelectric effect**; (solved by Einstein)

- **The Compton effect**; (solved by Compton)

- **Atomic spectra**; (solved by Bohr)

Blackbody radiation

The basis of blackbody radiation is that stuff emits radiation when heated. Examples are stars or a hotplate or a piece of metal being heated in a flame.

Initially as the stuff gets hot it turns red, then yellow, then blue and then white as the object gets hotter and hotter.

The blackbody is an idealized object that absorbs and emits all frequencies perfectly.

Now what was observed was the following spread of frequencies as a function of temperature. Note that $T_1 < T_2 < T_3$ and you see that the center frequency (color) changes as a function of temperature.

So to explain how these colors or center frequencies changed, Wein came up with his displacement law called today the "Wein displacement law". This happened around 1890 and empirically predicted how the peak moved with temperature.

Now what about the shape of the curve. Well, about the same time, Raleigh was working on this problem (around 1900). He came up with the following:

Imagine some sphere of radius k with volume

$$V_k = \frac{4}{3}\pi k^3$$

Now the volume of a given "mode" is $k_x k_y k_z$ where

$$\begin{aligned} k_x &= \frac{2\pi}{L_x} \\ k_y &= \frac{2\pi}{L_y} \\ k_z &= \frac{2\pi}{L_z} \end{aligned}$$

These relations come from boundary conditions and the factor of 2 comes from the special case of periodic boundary conditions (called Von Karman conditions). Basically for a function $sin(kL_x) = 0$ at a boundary the following is true $kL_x = n\pi$ where $k_x = \frac{n\pi}{L_x}$ and $n = 1, 2, 3 \ldots$

The number of modes N in a given sphere is

$$N = \frac{V_k}{k_x k_y k_z} = \frac{\frac{4}{3}\pi k^3}{8\pi^3} L_x L_y L_z$$

Multiply by 2 to account for two polarizations

$$N' = \frac{k^3 L_x L_y L_z}{3\pi^2}$$

Now consider the volume density ρ (divide the above expression by $L_zL_yL_z$)

$$\rho = \frac{k^3}{3\pi^2} \text{ (\# modes/unit volume)}$$

Now to get the frequency density, let $k = \frac{2\pi}{\lambda}$ where $\lambda = \frac{c}{\nu}$. Therefore $k = \frac{2\pi\nu}{c}$.

Then ρ becomes $\frac{\frac{8\pi^3\nu^3}{c^3}\left(\frac{1}{3\pi^2}\right)=8\pi\nu^3}{3c^3}$.

Now to get the frequency density

$$\rho^{'} = \frac{d\rho}{d\nu} = \frac{8\pi\nu^2}{c^3} \text{ (\# modes/unit volume/unit frequency)}$$

Next Raleigh multiplies $\rho^{'}$ by kT which is the classical average energy of his system ($< E >$)

$$< E >= \frac{\int_0^\infty Ee^{-\frac{E}{kT}}dE}{\int_0^\infty e^{-\frac{E}{kT}}dE} = kT$$

leading to

$$\boxed{u(\nu, T) = \left(\frac{8\pi\nu^2}{c^3}\right) kT} \tag{3.1}$$

Now this is called the Raleigh-Jeans Law.

So when you plot this function versus experimental data you get something which blows up quadratically with frequency. This is no good. No way-something is wrong. We can't have the infinite emission of UV light. This relation and derivation was re-checked by others and found to be formally correct using the physics known at the time. Hence the problem came to be known as the "Ultraviolet Catastrophe".

Now Wein who derived the Wein displacement law earlier decided to give it a try as well. Without going into what he did, Wein got his own expression shown below

$$\boxed{u(\nu, T) = A\nu^3 e^{-\frac{\beta\nu}{T}}} \tag{3.2}$$

where A and β are fudge factors for fitting purposes.

Now when you plot Wein's law you get a function which blows up a low frequencies. So this is no good either.

In summary, you have the Raleigh-Jeans and Wein laws giving functions which do a decent job fitting the experimental data on the high and low frequency sides respectively. But nothing which can fit the entire thing in one shot.

So how is this fixed? Well Planck came along and found a function that seemed to work pretty well. But to derive this expression he had to make some important (and controversial) assumptions along the way.

Contrary to classical physics, Planck postulated that the energy of radiation is discrete or "quantized". It comes along in integer amounts called "quanta".

$$E = nh\nu$$

where $n = 1, 2, 3 \ldots$ and h is a constant named after Planck himself.

So instead of

$$< E >= \frac{\int_0^\infty E e^{-\frac{E}{kT}} dE}{\int_0^\infty e^{-\frac{E}{kT}} dE}$$

he gets

$$\boxed{< E >= \frac{\sum_0^\infty nh\nu e^{-\frac{nh\nu}{kT}}}{\sum_0^\infty e^{-\frac{nh\nu}{kT}}}} \tag{3.3}$$

Therefore

$$\boxed{< E >= \frac{h\nu}{e^{\frac{h\nu}{kT}} - 1}} \tag{3.4}$$

Note that $\frac{1}{e^{\frac{h\nu}{kT}} - 1}$ is actually the Bose-Einstein distribution.

Now Planck takes $\rho^{'} = \frac{8\pi\nu^2}{c^3}$ and multiplies by his version of $< E >$ to get

$$\boxed{u(\nu, T) = \frac{8\pi\nu^2}{c^3} \left(\frac{h\nu}{e^{\frac{h\nu}{kT}} - 1} \right)} \tag{3.5}$$

which is today known as the Planck distribution in his honor.

Alternatively the Planck distribution can be written in other ways. For example, as a function of wavelength.

$$u(\lambda, T) = \frac{8\pi hc}{\lambda^5} \left(\frac{1}{e^{\frac{hc}{\lambda kT}} - 1} \right)$$

Now by fitting the experimental data, Planck was able to back out the value of his constant $h = 6.62 \cdot 10^{-34}$ Joule seconds.

So Planck was able to solve the problem of blackbody radiation by assuming that energies were quantized.

Now we should point out that at the time a lot of people did not think much of this and considered this result and success as a curiosity.

The photoelectric effect

The photoelectric effect is the observation that electrons are emitted when metals such as cesium are irradiated with light.

This phenomenon was discovered by Hertz in 1887. But apart from the experiment there were some odd observations about the phenomenon

- No electrons are ejected regardless of the incident light intenisty unless its frequency exceeds a threshold value characteristic of the metal
- Even at very low excitation intensities, electrons are ejected immediately from the metal if the frequency ν is greater than some threshold value.
- The kinetic energy of ejected electrons increases linearly with the frequency of the incident radiation.

You couldn't explain these observations classically. Inspired by Planck's success explaining blackbody radiation, Einstein tried and eventually succeeded in explaining the photoelectric effect in 1905.

He assumed that light was particle-like and called each particle a "photon." Then he said each photon carries a discrete energy $h\nu$ with it.

Now when each photon smacks the metal it gives all of its incident energy to an electron in the metal.

If $h\nu$ is greater than the metal's work function, the electron pops out and is ejected.

The excess energy carried away by the ejected electron is therefore the difference

$$KE = h\nu - w \tag{3.6}$$

where w is the metal's work function. This is a linear expression $y = mx + b$ with slope h and explains why the kinetic energy increases linearly with ν.

Finally, a fit to the line yields h in good agreement with the empirically derived fit value by Planck himself. This further solidified the idea of quantization.

Einstein won his Nobel Prize for this work.

Atomic spectra

It was known for a while that atoms have a characteristic emission spectrum. The emission spectrum generally consists of a series of lines with discrete frequencies.

Now for many years people tried to come up with some scheme to explain this line spectra, especially that of hydrogen which appeared pretty simple.

The first guy to get any sort of success was Balmer who developed an empirical formula to predict the correct line positions for hydrogen. This was done in 1885.

Next Rydberg generalized Balmer's formula to get his own version that nailed all of the hydrogen lines rather than a small subset like Balmer. His formula was

$$\boxed{\frac{1}{\lambda} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)} \tag{3.7}$$

where R is called the Rydberg constant and n_1 and n_2 are integers.

But this whole scheme was empirical. It was made up just to mathematically fit the data. We need a better understanding.

So now Bohr came into the picture and developed what is today known as the Bohr model of the atom. He developed this model by assuming that the angular momentum of an electron in hydrogen is quantized.

To derive his expression we need to equate the centripetal force of an electron with the Coulomb attraction between the electron and the positively charged nucleus.

$$\boxed{\frac{mv^2}{r} = \frac{q^2}{4\pi\epsilon_o r^2}} \tag{3.8}$$

The angular momentum of the electron is assumed to be quantized.

$$l = mvr = n\hbar$$

where $\hbar = \frac{h}{2\pi}$ and $n = 1, 2, 3\ldots$. Rearranging this yields $v = \frac{n\hbar}{mr}$ so that

$$\frac{mv^2}{r} = \frac{n^2\hbar^2}{mr^3}$$

leading to the equality

$$\begin{aligned}\frac{n^2\hbar^2}{mr^3} &= \frac{q^2}{4\pi\epsilon_o r^2}\\ \frac{n^2\hbar^2}{mr} &= \frac{q^2}{4\pi\epsilon_o}\end{aligned}$$

Solve for r to obtain

$$r = \frac{n^2\hbar^2}{m}\frac{4\pi\epsilon_o}{q^2} = \frac{4\pi\epsilon_o n^2\hbar^2}{mq^2}$$

where $n = 1, 2, 3\ldots.$ This ultimately yields

$$\boxed{r = \frac{4\pi\epsilon_o n^2\hbar^2}{mq^2}} \tag{3.9}$$

One can see that the Bohr orbits are quantized by an integer n.

Now the total energy is

$$E_{tot} = \frac{1}{2}mv^2 - \frac{q^2}{4\pi\epsilon_o r}$$

where $V(r) = \frac{q^2}{4\pi\epsilon_o r}$ and is the Coulomb potential.

Now since

$$\begin{aligned}\frac{mv^2}{r} &= \frac{q^2}{4\pi\epsilon_o r^2}\\ mv^2 &= \frac{q^2}{4\pi\epsilon_o r}\end{aligned}$$

leading to

$$\begin{aligned}E_{tot} &= \frac{1}{2}\left(\frac{q^2}{4\pi\epsilon_o r}\right) - \frac{q^2}{4\pi\epsilon_o r}\\ &= -\frac{1}{2}\left(\frac{q^2}{4\pi\epsilon_o r}\right)\\ &= -\frac{q^2}{8\pi\epsilon_o r}\end{aligned}$$

and finally

$$\boxed{E_{tot} = -\frac{q^2}{8\pi\epsilon_o r}} \tag{3.10}$$

where recall that $r = \frac{4\pi\epsilon_o n^2\hbar^2}{mq^2}$. This allows us to keep going and get an alternative expression for the energy.

$$\begin{aligned} E_{tot} &= -\frac{q^2}{8\pi\epsilon_o r}\frac{mq^2}{4\pi\epsilon_o n^2\hbar^2} \\ &= -\frac{mq^4}{32\pi^2\epsilon_o^2 n^2\hbar^2} \\ &= -\frac{mq^4}{4\epsilon_o^2 n^2 h^2} \end{aligned}$$

We are left with

$$\boxed{E_{tot} = -\frac{mq^4}{8\epsilon_o^2 h^2}\left(\frac{1}{n^2}\right)} \tag{3.11}$$

where $n = 1, 2, 3\ldots.$ So now the difference in energies is

$$\boxed{\Delta E = \frac{mq^4}{8\epsilon_o^2 h^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) = h\nu} \tag{3.12}$$

This looks familiar to the Rydberg empirically derived formula

$$\frac{1}{\lambda} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

where R was the Rydberg constant and $E = \frac{hc}{\lambda}$. From this we conclude that

$$\boxed{R = \frac{mq^4}{8\epsilon_o^2 c h^3}} \tag{3.13}$$

So Bohr was basically able to explain the discrete atomic spectra by making assumptions contrary to classical physics.

These defeats in turn began to signal the end of the classical physics heyday.

deBroglie wave-particle duality

So through the previous discussion on the photoelectric effect and black-body radiation we see that light isn't 100% wave-like. It has some particle character to it.

Around this time, with this idea in mind, deBroglie as part of his Ph. D. thesis came up with a hypothesis of the wave-particle duality for light and for matter. This wave-particle duality encompasses light, electrons, C60, other objects, and even macroscopic objects. Everything basically has both particle and wave-like characteristics.

The deBroglie hypothesis is basically reduced to one equation these days and is

$$\boxed{\lambda = \frac{h}{p}} \tag{3.14}$$

where λ is the deBroglie wavelength, h is Planck's constant and $p = mv$ is the momentum where m is the mass.

Now even though you and I have wave-like characteristics, our wavelengths are extremely small and as far as anyone is concerned we are best described by Newton's laws.

But the wave-like property of matter becomes important when you deal with small things. The best example is the electron and it is here with the electron that a lot of quantum mechanics takes place.

Finally 2 last points.

- deBroglie won the Nobel Prize in $\sim$ 1929 for this work
- The deBroglie hypothesis has been experimentally verified by experiments showing diffraction and inteference effects with electrons, C60 and other objects.

So matter as well as light has wave-like properties. This is the start of modern quantum chemistry and quantum mechanics.

Chapter 4

Fundamentals

Wavefunctions and such

Given the deBroglie wave-particle duality it turns out that we can mathematically express a particle like a wave using a "wavefunction" (usually denoted Ψ). This wavefunction replaces the classical concept of a trajectory and contains all the dynamical information about a system that you can know. Usually much of the work we will do here will be to find out what this wavefunction looks like given certain constraints on the system (called boundary conditions).

There is a probabilistic interpretation of the wavefunction called the Born interpretation. In this respect

$$\begin{aligned} |\Psi|^2 &= \Psi^*\Psi \text{ is considered as a probability density} \\ |\Psi|^2 dx &= \Psi^*\Psi dx \text{ is considered as a probability} \end{aligned}$$

Through these quantities one can determine the probability that the particle is somewhere. Note that from a physical perspective only $|\Psi|^2$ has some physical significance. Ψ can be real or imaginary or negative but $|\Psi|^2$ will be real and positive.

One consequence of the probabilistic interpretation of the wavefunction is that it must be normalized.

$$\int |\Psi|^2 dx = 1$$

This is because the probability of finding the particle somewhere must be unity. So generally you will see that in front of $\Psi(x,t)$ will be a constant N which ensures normalization is met. Physical particles therefore have normalizable wavefunctions, non-physical ones have wavefunctions that are not normalizable.

There are some important mathematical properties (or mathematical constraints) of the wavefunction described as follows

- Ψ must be "well behaved" in general
- Ψ must be finite (it does not blow up or show singularities. This constraint of course is related to being able to normalize the wavefunction. Can't do it if it goes nuts.)
- Ψ must be single valued. Obviously it doesn't make sense to have multiple probabilities at a given position.
- Ψ must be continuous.
- Ψ must have a first derivative (related to the previous statement)
- Ψ must have a second derivative (related to the previous, previous statement)
- Ψ must be integrable and hence normalizable (basically a consequence of 1 and 2)

Other properties to remember include

- normalization $\int |\Psi|^2 dx = 1$
- orthogonality $\int \Psi_1 \Psi_2 dx = 0$. Thus these two wavefunctions Ψ_1 and Ψ_2 have no mutual spatial overlap.

Observables

All dynamical information about the particle or system is contained in the wavefunction. This includes observables such as

- position
- momentum
- angular momentum
- energy

So while the wavefunction itself is not a measurable quantity, these observables are in principle.

In quantum mechanics, just like the particle is represented by a mathematical wavefunction, observables are represented by mathematical "operators".

An operator will act on a wavefunction to transform it into another function. Some examples of operators include

- x (multiply by x)
- $\frac{\partial}{\partial x}$ (take the partial derivative with respect to x)
- $\frac{\partial}{\partial t}$ (take the partial derivative with respect to time)

You will sometimes see operators denoted by a little hat on top of it. For example

- $\hat{x} = x$ operator (multiply by x)
- $\hat{y} = y$ operator (multiply by y)
- and so forth

Correspondence principle

In quantum mechanics all physical observables have corresponding operators. Two fundamental operators are the position operator $\hat{x}$ and the momentum operator $\hat{p}$.

- position operator, $\hat{x} = x$. (read as multiply by x)
- momentum operator, $\hat{p} = -i\hbar\nabla = -i\hbar\frac{\partial}{\partial x}$ (read as take the derivative with respect to x and multiply by $-i\hbar$)

All other operators can be constructured from combinations of these two fundamental operators. For example, for the kinetic energy operator (used to extract out the energy of the particle through its wavefunction)

$$\begin{aligned}
T &= \frac{p^2}{2m} \\
&= \frac{1}{2m}\left(-i\hbar\frac{\partial}{\partial x}\right)\left(-i\hbar\frac{\partial}{\partial x}\right) \\
&= \frac{1}{2m}\left(-\hbar^2\frac{\partial^2}{\partial x^2}\right) \\
&= -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}
\end{aligned}$$

This leads to

$$\boxed{T = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}} \tag{4.1}$$

For the potential energy $V(x)$ we have

$$\boxed{V(x) = V(x)} \tag{4.2}$$

Read this as multiply by $V(x)$.
For the total energy in 1D we have the operator $H = T + V$ where H is called the Hamiltonian operator.

$$\begin{aligned} H &= T + V \\ H &= -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x) \end{aligned}$$

Therefore

$$\boxed{H = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)} \tag{4.3}$$

This is the total energy operator called the Hamiltonian operator or Hamiltonian for short.
For the total energy in 3D

$$\begin{aligned} H &= \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m} + V(x,y,z) \\ &= \frac{1}{2m}\left(-i\hbar\frac{\partial}{\partial x}\right)\left(-i\hbar\frac{\partial}{\partial x}\right) + \frac{p_y^2}{2m} + \frac{p_z^2}{2m} + V(x,y,z) \\ &= -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} - \frac{\hbar^2}{2m}\frac{\partial^2}{\partial y^2} - \frac{\hbar^2}{2m}\frac{\partial^2}{\partial z^2} + V(x,y,z) \end{aligned}$$

This results in

$$\boxed{H = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + V(x,y,z)} \tag{4.4}$$

$$\boxed{H = -\frac{\hbar^2}{2m}\nabla^2} \tag{4.5}$$

where ∇^2 is called the Laplacian or "Del-squared" and

$$\nabla = \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}\right)$$

In addition $\Delta = \nabla^2$ (French)

So to summarize you can see that other operators can be built up from the fundamental operators $\hat{x}$ and $\hat{p}$.

Eigenvalues and eigenfunctions

Now a special class of function which when operated on yields itself again (may be multiplied by a constant or something) is called an eigenfunction (or eigenvector) of the operator. The constant that falls out is called an eigenvalue of the operator. For example, you could have

$$\frac{\partial}{\partial x}(e^{\alpha x}) = \alpha e^{\alpha x}$$

Here the function $e^{\alpha x}$ is an eigenfunction of the $\frac{\partial}{\partial x}$ operator and the constant α is an eigenvalue of the operator.

Expectation values

The average of mean value of an observable A is by definition

$$\boxed{< A >= \int \Psi^* \hat{A} \Psi dx} \tag{4.6}$$

This is called “sandwiching”.

In the special case that Ψ is an eigenfunction of the operator A

$$\hat{A}\Psi = a\Psi$$

Therefore

$$\begin{aligned} < A > &= \int \Psi^* \hat{A} \Psi dx \\ &= \int \Psi^* a \Psi dx \\ &= a \int \Psi^* \Psi dx \\ &= a \text{ since by normalization the integral is 1} \end{aligned}$$

Therefore

$$< A >= a$$

in the special case that Ψ is an eigenfunction of A.

Dirac Bra-Ket notation (a quick aside)

Dirac suggested a shorthand notation for writing and dealing with wavefunctions, operators and such. This new notation turns out to be easier and faster than the default calculus approach.

In this notation

- A wavefunction Ψ is denoted by $|\Psi >$ and is called a ket
- The complex conjugate Ψ^* is denoted by $< \Psi|$ and is called a bra

Bras and kets follow the rules of linear algebra

- $< a|b >=< b|a >^*$
- $|aA >= a|A >$ if a is a constant (a scalar)
- $< aA| = a^* < A|$

  Likewise
- $< A|bB + cC >= b < A|B > +c < A|C >$

Integrals are represented in the following fashion

$$\begin{aligned}
\int \Psi_1^* \Psi_1 dx &= < 1|1 >= 1 \text{ normalization} \\
\int \Psi_2^* \Psi_1 dx &= < 2|1 >= 0 \text{ orthogonality} \\
\int \Psi_1^* \hat{A} \Psi_1 dx &= < 1|\hat{A}|1 > \text{ Sandwiching} \\
\int \Psi_2^* \hat{A} \Psi_1 dx &= < 2|\hat{A}|1 > \text{ Sandwiching}
\end{aligned}$$

and so forth.

Operator math

Just as wavefunctions have to obey certain constraints, they are important restrictions on operators that represent observable quantities. This is called “linearity” and “hermiticity”

Linearity:

An operator $\hat{A}$ is linear for any constants α and β and wavefuncions $|f>$ and $|g>$ if

$$\hat{A}\left(\alpha|f> + \beta|g>\right) = \alpha\hat{A}|f> + \beta\hat{A}|g>$$

So the operator acting on the whole superposition wavefunction $\Psi_{tot} = \alpha|f> + \beta|g>$ is the same as the operator acting individually on the parts.

Hermiticity:

An operator $\hat{A}$ is Hermitian if its integrals obey the following relationship for all valid $|f>$ and $|g>$

$$\begin{aligned} \int \Psi_f^* \hat{A} \Psi_g dx &= \int \Psi_g^* \hat{A} \Psi_f dx \\ < f|\hat{A}|g >^* &= < g|\hat{A}|f > \end{aligned}$$

This restriction ensures that eigenvalues of $\hat{A}$ are all real-valued (as opposed to complex).

If its going to be observable in real life the number has to be real (not complex).

"Proof":

$|k>$ is an eigenfunction of $\hat{A}$ with eigenvalue k. Because $\hat{A}$ is Hermitian

$$\begin{aligned} < k|\hat{A}|k >^* &= < k|\hat{A}|k > \\ k^* &= k \end{aligned}$$

Therefore k is real valued.

Furthermore, eigenfunctions of a Hermitian operator associated with different eigenvalues are all orthogonal.

"Proof":

$$\begin{aligned} < j|\hat{A}|k >^* &= < k|\hat{A}|j > \\ k < j|k >^* &= j < k|j > \text{ where } < k|j > = < j|k >^* \\ (k - j) < k|j > &= 0 \end{aligned}$$

Since $k \neq j$ (they are different eigenvalues)

$$< k|j > = 0$$

More on operators

$$\hat{A}|\Psi>=|\hat{A}\Psi>=|\Psi^{'}>$$

so that

$$\begin{aligned}|\Psi^{'}> &\longleftrightarrow <\Psi^{'}| \\ |\hat{A}\Psi> &\longleftrightarrow <\hat{A}\Psi| \\ \hat{A}|\Psi> &\longleftrightarrow <\Psi|\hat{A}^{\dagger}\end{aligned}$$

where $\hat{A}^{\dagger}$ is called the adjoint of $\hat{A}$ operator.

More games with the adjoint

1)

$$\begin{aligned}<\phi|\hat{A}|\Psi> &= <\phi|\hat{A}\Psi> \\ &= <\hat{A}\Psi|\phi>^{*} \\ &= <\Psi|\hat{A}^{\dagger}|\phi>^{*}\end{aligned}$$

Therefore

$$\boxed{<\phi|\hat{A}|\Psi>=<\Psi|\hat{A}^{\dagger}|\phi>^{*}} \tag{4.7}$$

of course if $A=A^{\dagger}$ then A is Hermitian.

2)

$$\boxed{<\phi|\hat{A}|\Psi>=<\phi|\hat{A}\Psi>} \tag{4.8}$$

$$\boxed{<\phi|\hat{A}|\Psi>=<\hat{A}^{\dagger}\phi|\Psi>} \tag{4.9}$$

The first expression reflects operation on the right. The second expression reflects operating on the left.

3)

$$\boxed{(\hat{A}\hat{B})^{\dagger}=\hat{B}^{\dagger}\hat{A}^{\dagger}} \tag{4.10}$$

Proof: Let

$$\begin{aligned}|\phi> &= (\hat{A}\hat{B})|\Psi> \\ &= \hat{A}|\hat{B}\Psi>\end{aligned}$$

Take adjoint now

$$\begin{aligned} \hat{A}|\hat{B}\Psi > &\rightarrow < B\Psi|\hat{A}^{\dagger} \\ \hat{A}\hat{B}|\Psi > &\rightarrow < \Psi|\hat{B}^{\dagger}\hat{A}^{\dagger} \\ &\ \text{Call } \hat{C} = \hat{A}\hat{B} \text{ or } \hat{C}^{\dagger} = \hat{B}^{\dagger}\hat{A}^{\dagger} \text{ resulting in} \\ \hat{C}|\Psi > &\rightarrow < \Psi|\hat{C}^{\dagger} \end{aligned}$$

This ends up with

$$\boxed{(\hat{A}\hat{B})^{\dagger} = \hat{B}^{\dagger}\hat{A}^{\dagger}} \tag{4.11}$$

4) If $\hat{A}$ and $\hat{B}$ are Hermitian ($\hat{A} = \hat{A}^{\dagger}$ and $\hat{B} = \hat{B}^{\dagger}$)

$$(\hat{A}\hat{B})^{\dagger} = \hat{B}^{\dagger}\hat{A}^{\dagger} = \hat{B}\hat{A} = \hat{A}\hat{B} + [\hat{B}, \hat{A}]$$

This results in the relationship where $[\hat{B}, \hat{A}]$ is called the “commutator” of the two operators. This will be introduced in the next section.

$$\boxed{(\hat{A}\hat{B})^{\dagger} = \hat{A}\hat{B} + [\hat{B}, \hat{A}]} \tag{4.12}$$

Commutators

A wavefunction Ψ with a characteristic well-defined value of some observable quantity is an eigenfunction of the corresponding operator. However, this Ψ does not have to have a characteristic value of any other observable.

For a Ψ to have a characteristic value of 2 observables simultaneously, the corresponding operators must “commute”

Definition of “commute”

The action of the two operators say $\hat{A}$ and $\hat{B}$ taken in succession on any Ψ is identical to the action of the operators taken in reverse order.

$$\hat{A}\hat{B} = \hat{B}\hat{A} \tag{4.13}$$

or equivalently that the “commutator” of the two operators equals zero.

Definition of "commutator"

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

A special case is

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

which occurs when $\hat{A}$ and $\hat{B}$ commute.

Now if such a Ψ exists then it is an eigenfunction of both operators. For example

$$\begin{aligned}
\hat{A}(\hat{B}|\beta >) &= \hat{A}\beta|\beta >= \beta\hat{A}|\beta > \\
\text{But now if } \hat{A}\hat{B} = \hat{B}\hat{A} \text{ then} & \\
\hat{A}\hat{B}|\beta > &= \hat{B}\hat{A}|\beta > \\
\beta\hat{A}|\beta > &= \hat{B}(\hat{A}|\beta >) \\
\text{which means that } (\hat{A}|\beta >) \text{ is an} & \\
\text{eigenfunction of } \hat{B}, \text{ call it } |\beta^{'} > & \\
&= \hat{B}|\beta^{'} > \\
&= \beta|\beta^{'} >
\end{aligned}$$

This implies that $|\beta >$ is an eigenfunction of $\hat{A}$. Hence $|\beta >$ is an eigenfunction of both $\hat{A}$ and $\hat{B}$ if they commute.

Alternative derivation

Claim that if $|\beta >$ is an eigenfunction of $\hat{B}$

$$\hat{B}|\beta >= \beta|\beta >$$

Then if $\hat{A}$ and $\hat{B}$ commute (i.e. $[\hat{B}, \hat{A}] = 0$), $|\hat{A}\beta >$ is also an eigenfunction of $\hat{B}$ with eigenvalue β. To illustrate:

$$\begin{aligned}
\hat{B}|\hat{A}\beta > &= \hat{B}\hat{A}|\beta >= (\hat{A}\hat{B} + [\hat{B}, \hat{A}])|\beta > \\
\text{since } [\hat{B}, \hat{A}] = 0 & \\
&= \hat{A}\hat{B}|\beta > \\
&= \beta(\hat{A}|\beta >) \\
&= \beta|\hat{A}\beta >
\end{aligned}$$

One therefore sees that

$$\boxed{\hat{B}|\hat{A}\beta >= \beta|\hat{A}\beta >} \tag{4.14}$$

Again this implies that $|\beta >$ is an eigenfunction of $\hat{A}$.

Conversely, if $\hat{A}$ and $\hat{B}$ do not commute ($[\hat{A}, \hat{B}] \neq 0$), you cannot specify the eigenvalues of both simultaneously (only one or the other). This is the origin of the uncertainty principle, which we will discuss later in more detail.

To illustrate this locally however, $\hat{x}$ and $\hat{p}$ do not commute.

Proof: (note that when working with operators its easier to have an imaginary test function to work on. otherwise it is easy to get confused.)

$$\begin{aligned}
[\hat{x}, \hat{p}]|\Psi > &= (\hat{x}\hat{p} - \hat{p}\hat{x})|\Psi > \\
&= \hat{x}\hat{p}|\Psi > -\hat{p}\hat{x}|\Psi > \\
&= -i\hbar\hat{x}\frac{d|\Psi >}{dx} + i\hbar\frac{d}{dx}(x|\Psi >) \\
&= i\hbar\left[-x\frac{d|\Psi >}{dx} + x\frac{d|\Psi >}{dx} + |\Psi >\right] \\
&= i\hbar|\Psi >
\end{aligned}$$

Resulting in

$$[\hat{x}, \hat{p}]|\Psi >= i\hbar|\Psi > \tag{4.15}$$

or alternatively that

$$\boxed{[x, p] = i\hbar} \tag{4.16}$$

This value is non-zero showing that $\hat{x}$ and $\hat{p}$ do not commute. And as advertised earlier this will lead to the Uncertainty principle

$$\boxed{\Delta x \Delta p \geq \tfrac{\hbar}{2}} \tag{4.17}$$

Furthermore, given 2 commuting observables $\hat{A}$ and $\hat{B}$ it is always possible to construct an orthonormal basis with eigenstates common to both $\hat{A}$ and $\hat{B}$.

Additional commutator math

Before we go on we will want to summarize some important commutator relations

- $[\hat{A}, \hat{A}] = 0$
- $[\hat{A}, \hat{B}] = -[\hat{B}, \hat{A}]$
- $[\hat{A}, \hat{B}\hat{C}] = [\hat{A}, \hat{B}]\hat{C} + \hat{B}[\hat{A}, \hat{C}]$
- $[\hat{A}\hat{B}, \hat{C}] = \hat{A}[\hat{B}, \hat{C}] + [\hat{A}, \hat{C}]\hat{B}$
- $[\hat{A}, \hat{B} + \hat{C}] = [\hat{A}, \hat{B}] + [\hat{A}, \hat{C}]$
- $[\hat{A}, b\hat{B}] = b[\hat{A}, \hat{B}]$
- $\Big[\hat{A}, [\hat{B}, \hat{C}]\Big] = [\hat{A}, \hat{B}\hat{C}] - [\hat{A}, \hat{C}\hat{B}]$
- $[\hat{A} + \hat{B}, \hat{C} + \hat{D}] = [\hat{A}, \hat{C}] + [\hat{A}, \hat{D}] + [\hat{B}, \hat{C}] + [\hat{B}, \hat{D}]$

Examples

Evaluate $[\hat{p}, \hat{x}^2]$. Remember to add some dummy wavefunction Ψ to help out.

$$\begin{aligned}
[\hat{p}, \hat{x}\hat{x}]\Psi &= \hat{p}\hat{x}\hat{x} - \hat{x}^2\hat{p}\Psi \\
\text{where } \hat{p} = -i\hbar\frac{d}{dx} & \\
&= -i\hbar\frac{d}{dx}(\hat{x}^2\Psi) - \hat{x}^2\frac{d\Psi}{dx}(-i\hbar) \\
&= -i\hbar\left[\hat{x}^2\frac{d\Psi}{dx} + 2\hat{x}\Psi\right] + i\hbar\hat{x}^2\frac{d\Psi}{dx} \\
&= i\hbar\left[-\hat{x}^2\frac{d\Psi}{dx} - 2\hat{x}\Psi + \hat{x}^2\frac{d\Psi}{dx}\right] \\
&= -2i\hbar\hat{x}\Psi
\end{aligned}$$

Therefore we conclude that

$$\boxed{[\hat{p}, \hat{x}^2] = -2i\hbar\hat{x}} \tag{4.18}$$

Evaluate $[\hat{p}^2, \hat{x}]$. Remember to add some dummy wavefunction Ψ to help out.

$$
\begin{aligned}
[\hat{p}^2, \hat{x}]\Psi &= (\hat{p}^2\hat{x} - \hat{x}\hat{p}^2)\Psi \\
&= \hat{p}^2\hat{x}\Psi - \hat{x}\hat{p}^2\Psi \\
&= -i\hbar\frac{d}{dx}\left[-i\hbar\frac{d}{dx}(x\Psi)\right] - \hat{x}\frac{d^2}{dx^2}(-i\hbar)^2 \\
&= -\hbar^2\frac{d}{dx}\left[x\frac{d\Psi}{dx} + \Psi\right] + \hbar^2 x\frac{d^2\Psi}{dx^2} \\
&= -\hbar^2\left[x\frac{d^2\Psi}{dx^2} + \frac{d\Psi}{dx} + \frac{d\psi}{dx}\right] + \hbar^2 x\frac{d^2\Psi}{dx^2} \\
&= -\hbar^2\left[x\frac{d^2\Psi}{dx^2} + 2\frac{d\Psi}{dx}\right] + \hbar^2 x\frac{d^2\Psi}{dx^2} \\
&= -\hbar^2 x\frac{d^2\Psi}{dx^2} - 2\hbar^2\frac{d\Psi}{dx} + \hbar^2 x\frac{d^2\Psi}{dx^2} \\
&= -2\hbar^2\frac{d\Psi}{dx} \\
&= \left[-2\hbar^2\frac{d}{dx}\right]\Psi \\
&= \left[\frac{2\hbar^2}{i\hbar}(-i\hbar)\frac{d}{dx}\right]\Psi \\
&= -2i\hbar\hat{p}\Psi
\end{aligned}
$$

Resulting in

$$\boxed{[\hat{p}^2, \hat{x}] = -2i\hbar\hat{p}} \tag{4.19}$$

The Uncertainty Principle

Heisenberg's Uncertainty Principle follows from a non-zero commutator. Better yet, we claim that there is an uncertainty principle whenever there are non-commuting operators.

To illustrate, suppose we have two Hermitian operators $\hat{A}$ and $\hat{B}$ such that $[\hat{A}, \hat{B}] = i\hat{C}$ where $\hat{C}$ is also Hermitian but $i\hat{C}$ is anti-Hermitian. Consider the uncertainty

$$(\Delta A)^2 =< \Psi|(\hat{A} - \bar{A})(\hat{A} - \bar{A})|\Psi >$$

where $\bar{A} =< A >=< \Psi|\hat{A}|\Psi >$. We desire to evaluate the product of the uncertainties in $\hat{A}$ and $\hat{B}$

$$\begin{aligned} & <\Psi|(\hat{A}-\bar{A})(\hat{A}-\bar{A})|\Psi><\Psi|(\hat{B}-\bar{B})(\hat{B}-\bar{B})|\Psi> \\ \geq & <\Psi|(\hat{A}-\bar{A})(\hat{B}-\bar{B})|\Psi><\Psi|(\hat{B}-\bar{B})(\hat{A}-\bar{A})|\Psi> \end{aligned}$$

This relation arises from something called the Schwarz Inequality. Furthermore we "know" that

$$\begin{aligned} (\hat{A}-\bar{A})(\hat{B}-\bar{B}) &= \frac{1}{2}[(\hat{A}-\bar{A})(\hat{B}-\bar{B})+(\hat{B}-\bar{B})(\hat{A}-\bar{A})+i\hat{C}] \\ &= \frac{1}{2}\left[(\hat{A}-\bar{A})(\hat{B}-\bar{B})+(\hat{B}-\bar{B})(\hat{A}-\bar{A})+[\hat{A},\hat{B}]\right] \end{aligned}$$

"Proof"

Don't have any real proof of this equality but we can show that they are equivalent. For simplicity in notation let $\bar{A}=a$ and $\bar{B}=b$. Remember though that a and b are just numbers, not operators. Also always remember to preserve the order of operation when dealing with operators. They matter.

$$\begin{aligned} &= \frac{1}{2}\left[(\hat{A}-a)(\hat{B}-b)+(\hat{B}-b)(\hat{A}-a)+i\hat{C}\right] \\ &= \frac{1}{2}[\hat{A}\hat{B}-b\hat{A}-a\hat{B}+ab+\hat{B}\hat{A}-a\hat{B}-b\hat{A}+ab+i\hat{C}] \\ &= \frac{1}{2}[\hat{A}\hat{B}+\hat{B}\hat{A}+2ab-2b\hat{A}-2a\hat{B}+i\hat{C}] \\ &= \text{where } i\hat{C}=[\hat{A},\hat{B}]=\hat{A}\hat{B}-\hat{B}\hat{A} \\ &= \frac{1}{2}[\hat{A}\hat{B}+\hat{B}\hat{A}+2ab-2b\hat{A}-2a\hat{B}+\hat{A}\hat{B}-\hat{B}\hat{A}] \\ &= \frac{1}{2}[2\hat{A}\hat{B}+2ab-2b\hat{A}-2a\hat{B}] \\ &= \hat{A}\hat{B}+ab-b\hat{A}-a\hat{B} \\ &= \hat{A}\hat{B}-b\hat{A}-a\hat{B}+ab \\ &= (\hat{A}-a)(\hat{B}-b) \end{aligned}$$

which shows the equivalence of the the two expressions.

So now we know that

$$(\hat{A}-\bar{A})(\hat{B}-\bar{B})=\left[\frac{(\hat{A}-\bar{A})(\hat{B}-\bar{B})+(\hat{B}-\bar{B})(\hat{A}-\bar{A})}{2}\right]+\frac{i\hat{C}}{2}$$

or

$$\boxed{(\hat{A}-\bar{A})(\hat{B}-\bar{B})=\hat{F}+\tfrac{i\hat{C}}{2}} \tag{4.20}$$

By the same token

$$\boxed{(\hat{B}-\bar{B})(\hat{A}-\bar{A})=\hat{F}-\tfrac{i\hat{C}}{2}} \tag{4.21}$$

Now using these two relations, the Schwarz inequality becomes

$$\begin{aligned}
(\Delta A)^2(\Delta B)^2 &\geq <\Psi|\hat{F}+\frac{i\hat{C}}{2}|\Psi><\Psi|\hat{F}-\frac{i\hat{C}}{2}|\Psi> \\
(\Delta A)^2(\Delta B)^2 &\geq [<\Psi|\hat{F}|\Psi>+\frac{i}{2}<\Psi|\hat{C}|\Psi>][<\Psi|\hat{F}|\Psi>-\frac{i}{2}<\Psi|\hat{C}|\Psi>] \\
(\Delta A)^2(\Delta B)^2 &\geq \\
& [<\Psi|\hat{F}|\Psi>^2-\frac{i}{2}<\Psi|\hat{F}|\Psi><\Psi|\hat{C}|\Psi> \\
&+ \frac{1}{4}<\Psi|\hat{C}|\Psi>^2+\frac{i}{2}<\Psi|\hat{C}|\Psi><\Psi|\hat{F}|\Psi>] \\
(\Delta A)^2(\Delta B)^2 &\geq \left[<\Psi|\hat{F}|\Psi>^2+\frac{1}{4}<\Psi|\hat{C}|\Psi>^2\right]
\end{aligned}$$

Now in the minimum case $<\Psi|\hat{F}|\Psi>=0$ such that

$$\boxed{(\Delta A)^2(\Delta B)^2 \geq \tfrac{1}{4}<\Psi|\hat{C}|\Psi>^2} \tag{4.22}$$

Let $<\Psi|\hat{C}|\Psi>=c$ where c is some scalar number. Then

$$(\Delta A)^2(\Delta B)^2 \geq \frac{c}{4}$$

such that

$$\boxed{(\Delta A)(\Delta B) \geq \tfrac{c^{'}}{2}} \tag{4.23}$$

This is the generalized uncertainty principle. Note that if $c^{'}=\hbar$ then we come back to the Heisenberg uncertainty principle for $\Delta A=\Delta x$ and $\Delta B=\Delta p$.

Motivating the uncertainty principle, not using commutators though

Consider a plane wave of monochromatic light.

$$\epsilon(x,t) \propto e^{ikx-i\omega t}$$

where $k = \frac{2\pi}{\lambda}$ and $\omega = kc$

Now generalize this to a linear superposition of different plane waves

$$\epsilon(x,t) \propto a_1 e^{ik_1x-i\omega_1 t} + a_2 e^{ik_2x-i\omega_2 t} + \ldots$$

Keep generalizing this and now consider a continuous distribution

$$\epsilon(x,t) \propto \int \epsilon(k) e^{ikx-i\omega t} dk$$

where $\epsilon(k)$ is a distribution of k values. Our job now is to find out what $\epsilon(k)$ looks like.

Recall the Fourier transform relations

$$\epsilon(x,0) \propto \int \epsilon(k) e^{ikx} dk \text{ Forward Fourier transform}$$
$$\epsilon(k) \propto \int \epsilon(x,0) e^{-ikx} dx \text{ Inverse Fourier transform}$$

This shows that $\epsilon(k)$ is just the inverse Fourier tranform of $\epsilon(x,0)$ which is the function of the wave in real space.

Now suppose that we put an "envelope" function $f(x)$ on top of our plane wave to define $\epsilon(x,0)$. We really measure in real life the intensity of the wave.

$$I(x,0) = |\epsilon(x,0)|^2 \propto f^2(x)$$

For convenience let's make our envelope Gaussian with a width of Δx.

$$\begin{aligned} |\epsilon(x,0)|^2 &\propto e^{-\frac{x^2}{2\Delta x^2}} \\ &\propto \left(e^{-\frac{x^2}{4\Delta x^2}}\right)\left(e^{-\frac{x^2}{4\Delta x^2}}\right) \end{aligned}$$

so that

$$\boxed{\epsilon(x,0) \propto e^{ik_o x} e^{-\frac{x^2}{4\Delta x^2}}} \qquad (4.24)$$

Now what are the distribution of frequencies for the Gaussian pulse (Find $|\epsilon(k)|^2$)? Well

$$
\begin{aligned}
\epsilon(k) &\propto \int \epsilon(x,0)e^{-ikx}dx \\
&\propto \int e^{ik_o x}e^{-\frac{x^2}{4\Delta x^2}}e^{-ikx}dx \\
&\propto \int e^{i(k_o-k)x}e^{-\frac{x^2}{4\Delta x^2}}dx \\
&\quad \text{let } y = \frac{x}{2\Delta x} \text{ such that } y^2 = \frac{x^2}{4\Delta x^2} \text{ and } dx = 2\Delta x dy \\
&\propto \int e^{-i(k_o-k)x}e^{-y^2}dy(2\Delta x) \\
&\propto \int 2\Delta x e^{-i(k_o-k)2\Delta x y}e^{-y^2}dy \\
&\propto 2\Delta x \int e^{-i2\Delta x(k_o-k)y}e^{-y^2}dy \\
&\propto 2\Delta x \int e^{-2i\Delta x(k_o-k)y}e^{-y^2}dy \\
&\quad \text{call } -2i\Delta x(k_o-k)y = ia \\
&\quad \text{where } a = 2\Delta x(k_o-k) \text{ for simplicity} \\
&\propto 2\Delta x \int e^{-iay}e^{-y^2}dy \\
&\quad \text{complete the square in the exponent} \\
&\propto 2\Delta x \int e^{-[(y+\frac{ia}{2})^2-\frac{i^2a^2}{4}]}dy \\
&\propto 2\Delta x e^{\frac{i^2a^2}{4}} \int e^{-(y+\frac{ia}{2})^2}dy \\
&\quad \text{let } z = (y+\frac{ia}{2}) \text{ and } dz = dy \\
&\propto 2\Delta x e^{\frac{-a^2}{4}} \int e^{-z^2}dz \\
&\quad \text{from our knowledge of Gaussian integrals we know the integral is } \sqrt{\pi} \\
&\propto 2\Delta x\sqrt{\pi}e^{\frac{-a^2}{4}} \\
&\propto 2\Delta x\sqrt{\pi}e^{-\frac{1}{4}\left(4\Delta x^2(k_o-k)^2\right)} \\
&\propto 2\Delta x\sqrt{\pi}e^{-\Delta x^2(k_o-k)^2}
\end{aligned}
$$

Leaving

$$\boxed{\epsilon(k) \propto 2\Delta x\sqrt{\pi}e^{-\Delta x^2(k_o-k)^2}} \tag{4.25}$$

Now $|\epsilon(k)|^2 \propto e^{-2\Delta x^2(k_o-k)^2}$ Convert this to Gaussian form.

$$\begin{aligned}
e^{-2\Delta x^2(k_o-k)^2} &= e^{-\frac{(k_o-k)^2}{2\Delta k^2}} \\
\text{therefore} & \\
2\Delta x^2 &= \frac{1}{2\Delta k^2} \\
\Delta x^2 \Delta k^2 &= \frac{1}{4}
\end{aligned}$$

or

$$\boxed{\Delta x \Delta k = \tfrac{1}{2}} \tag{4.26}$$

Now since

$$\begin{aligned}
\omega = kc &\;\; \rightarrow \;\; \Delta\omega = c\delta k \\
x = ct &\;\; \rightarrow \;\; \Delta x = c\Delta t
\end{aligned}$$

you get from the second expression $c = \frac{\Delta x}{\Delta t}$ and this can be substituted into the first expression to get

$$\boxed{\Delta\omega\Delta t = \tfrac{1}{2}} \tag{4.27}$$

More generally speaking though

$$\boxed{\Delta\omega\Delta t \geq \tfrac{1}{2}} \tag{4.28}$$

This is the uncertainty relation for an arbitrary pulse shape. Note also that $E = \hbar\omega$ so that one can perhaps get a more familiar looking Uncertainty relation.

$$\boxed{\Delta E \Delta t \geq \tfrac{\hbar}{2}} \tag{4.29}$$

We can keep going to get other variations of the Uncertainty relation. Since $p = \hbar k$ one has $\Delta p = \hbar\Delta k$ and $\Delta k = \frac{1}{2\Delta x}$ from the previous uncertainty relation all resulting in $\Delta p = \frac{\hbar}{2\Delta x}$.

$$\boxed{\Delta p \Delta x = \tfrac{\hbar}{2}} \tag{4.30}$$

More generally speaking though

$$\boxed{\Delta p \Delta x \geq \frac{\hbar}{2}} \tag{4.31}$$

This is the general form of the Heisenberg Uncertainty principle that you will see.

But the main take home message apart from the various forms of the Uncertainty principle is that short laser pulses contain a lot of colors and conversely longer ones have less- they are more monochromatic.

Chapter 5

Schrödinger Equation

The time independent Schrödinger equation

The general form of the Schrodinger equation which we will need to solve many times is

$$\boxed{i\hbar\tfrac{\partial}{\partial t}\Psi(r,t) = H\Psi(r,t)} \tag{5.1}$$

where H is the Hamiltonian operator. Alternatively

$$i\hbar\frac{\partial}{\partial t}\Psi(r,t) = \left[-\frac{\hbar^2}{2m}\nabla^2 + V\right]\Psi(r,t)$$

where V is some generic potential.

This equation derived by Schrodinger describes the wavefunction of the particle and hence is pretty important. The general form of the Schrodinger equation has time dependence as you see above. However if can be shown that there is a time independent form of the equation also called the Schrodinger equation. To distinguish these two equations the former is often referred to as the time-dependent Schrodinger equation. Note that one typically deals with the time-independent version for the first semester of quantum and then get into the time-dependent version in the second semsester.

To obtain the time-independent version of the Schrodinger equation assume that V does not depend on time. It is only dependent on position $V \to V(r)$. We have

$$i\hbar\frac{\partial}{\partial t}\Psi(r,t) = \left(-\frac{\hbar^2\nabla^2}{2m} + V\right)\Psi(r,t)$$

Note that the left side has time dependence while the right side only has a spatial dependence. Look for solutions of the form

$$\begin{aligned} \Psi(r,t) &= \Psi(r)f(t) \\ &= \Psi f \text{ shorthand expression} \end{aligned}$$

We now have

$$\begin{aligned} i\hbar\frac{\partial}{\partial t}(\Psi f) &= -\frac{\hbar^2\nabla^2}{2m}\Psi f + V\Psi f \\ i\hbar\Psi\frac{\partial f}{\partial t} &= -\frac{\hbar^2 f}{2m}\nabla^2\Psi + V\Psi f \\ \frac{i\hbar\Psi}{f}\frac{\partial f}{\partial t} &= \frac{1}{\Psi}\left[-\frac{\hbar^2\nabla^2}{2m}\Psi + V\Psi\right] \end{aligned}$$

Note that the left hand side is independent of position and the right hand side is independent of time. Both sides must equal a constant (call it ϵ) in order to be consistent. It turns out that this constant is the system eigenenergy which is why we are calling it ϵ already.

Left hand side

$$\begin{aligned} \frac{i\hbar}{f}\frac{\partial f}{\partial t} &= \epsilon \\ \frac{1}{f}\frac{\partial f}{\partial t} &= \frac{\epsilon}{i\hbar} \\ \frac{1}{f}\frac{\partial f}{\partial t} &= \frac{-i\epsilon}{\hbar} \\ lnf &= -\frac{i\epsilon t}{\hbar} \\ & \text{note that there is a constant of integration} \\ & \text{but we ignore it here} \end{aligned}$$

This results in

$$\boxed{f = e^{\frac{-i\epsilon t}{\hbar}}} \tag{5.2}$$

The form of the function is exponential but it has an imaginary exponent. So what does this mean? Well, it means that one has plane waves. Note that $e^{ikx} = coskx + isinkx$.

Right hand side

$$\begin{aligned}\frac{1}{\Psi}\left[-\frac{\hbar^2\nabla^2\Psi}{2m}+V\Psi\right] &= \epsilon \\ H\Psi &= \epsilon\Psi\end{aligned}$$

This expression is something that we are familiar with. Its our favorite eigenvalue and eigenvector problem.

Summary

So putting everything together we have the full form of the wavefunction (both the time-dependent and time-independent parts).

$$\boxed{\Psi = \Psi(r)e^{-\frac{i\epsilon t}{\hbar}}} \tag{5.3}$$

Recall that additional constraints on $\Psi(r)$ include

- $\Psi(r)$ is finite
- $\Psi(r)$ is continuous
- $\Psi^{'}(r)$ is continuous

Furthermore, boundary conditions on the wavefunction will induce quantization on the energies ϵ as well as the mathematical form of the wavefunction. Here you will note that typically the first semester of quantum mechanics is spent solving the time independent Schrodinger equation for a number of different situation and boundary conditions. These problems are referred to as model problems and will be described in the next sections.

What do we mean

What exactly did we mean above. Well let's go back to the full time-dependent Schrodinger equation

$$i\hbar\frac{\partial}{\partial t}\Psi(r,t) = H\Psi(r,t)$$

where we just found that

$$\Psi(r,t) = \Psi(r)e^{-\frac{i\epsilon t}{\hbar}}$$

Replace this into the Schrodinger equation and evaluate.

$$\begin{aligned}
i\hbar\frac{\partial}{\partial t}\left[\Psi(r)e^{\frac{-i\epsilon t}{\hbar}}\right] &= H\Psi(r)e^{\frac{-e\epsilon t}{\hbar}} \\
i\hbar\Psi(r)\frac{\partial}{\partial t}\left[e^{-\frac{i\epsilon t}{\hbar}}\right] &= H\Psi(r)e^{\frac{-i\epsilon t}{\hbar}} \\
i\hbar\left(-\frac{i\epsilon}{\hbar}\right)\Psi(r)e^{-\frac{i\epsilon t}{\hbar}} &= H\Psi(r)e^{-i\frac{\epsilon t}{\hbar}} \\
i\hbar\left(-\frac{i\epsilon}{\hbar}\right)\Psi(r) &= H\Psi(r)
\end{aligned}$$

leaving

$$\boxed{H\Psi(r) = \epsilon\Psi(r)} \tag{5.4}$$

which is the time independent Schrodinger equation or our familiar eigenvalue and eigenvector problem. We will solve this equation a bunch of times for a number of model systems. Later on we will go back and deal more directly with the time dependent Schrodinger equation.

Some relevant applications of the time independent Schrodinger equation include

- particle in a box (absorption)
- harmonic oscillator (vibrations)
- rigid rotor (rotational spectra)

Chapter 6

Particle in a 1D Infinite Box

Picture the following potential with infinite walls. The potential is therefore

- $V = \infty (x \leq 0)$
- $V = 0 (0 < x < a)$
- $V = \infty (x \geq a)$

where a is the width of the box.

The Schrodinger equation is

$$\boxed{-\tfrac{\hbar^2}{2m}\tfrac{d^2\Psi}{dx^2} + V\Psi = \epsilon\Psi} \tag{6.1}$$

Let's rearrange this equation a little bit

$$\begin{aligned} -\frac{\hbar^2}{2m}\frac{d^2\Psi}{dx^2} &= \epsilon\Psi \\ \frac{d^2\Psi}{dx^2} &= -\frac{2m\epsilon}{\hbar^2}\Psi \\ \frac{d^2\Psi}{dx^2} + k^2\Psi &= 0 \\ \text{where } k^2 = \frac{2m\epsilon}{\hbar^2} & \end{aligned}$$

The general solutions to this last equation are

$$\boxed{\Psi = Ae^{ikx} + Be^{-ikx}} \tag{6.2}$$

where it is understood that Ae^{ikx} is a left going wave and that e^{-ikx} is a right going wave. Note that this is because we implicitly have assumed the $e^{\frac{-i\epsilon t}{\hbar}}$ part of the full time dependent wavefunction.

Now to get our particular solution we must apply boundary conditions intrinsic to the problem.

Boundary conditions

- $\Psi(0) = 0$
- $\Psi(a) = 0$

When one applies the boundary conditions we have the following equations.

$$\begin{aligned}\Psi(0) &= A + B = 0\\ \Psi(a) &= Ae^{ika} + Be^{-ika} = 0\end{aligned}$$

From the first expression we have

$$B = -A$$

From the second expression and the above result we have

$$Ae^{ika} - Ae^{-ika} = 0$$

or

$$\begin{aligned}2iA\left(\frac{e^{ika} - e^{-ika}}{2i}\right) &= 0\\ 2iAsinka &= 0\end{aligned}$$

So for this last expression to be true, we either have the trivial solution ($A = 0$) or ($ka = n\pi$) where n is some integer. Since we don't want the trivial solution we are left with

$$ka = n\pi$$

resulting in

$$\boxed{k = \tfrac{n\pi}{a}} \tag{6.3}$$

Energies

But now recall that we had found earlier that $k = \sqrt{\frac{2m\epsilon}{\hbar^2}}$. Therefore

$$\begin{aligned}\sqrt{\frac{2m\epsilon}{\hbar^2}} &= \frac{n\pi}{a}\\ \epsilon &= \frac{n^2\pi^2}{a^2}\frac{\hbar^2}{2m}\end{aligned}$$

We then have

$$\boxed{\epsilon = \frac{n^2h^2}{8ma^2}} \tag{6.4}$$

Wavefunctions

Now go back and find the relevant wavefunctions

$$\Psi = A(e^{ikx} - e^{-ikx})$$

Resulting in

$$\boxed{\Psi = 2iAsinkx} \tag{6.5}$$

Now we must normalize the wavefunction over the interval from $0 \to a$. Let $N = 2iA$

$$\begin{aligned}
N^2 \int_0^a \Psi^* \Psi dx &= 1 \\
N^2 \int_0^a sin^2kxdx &= 1 \\
\text{where } sin^2kx = \frac{1}{2}(1 - cos2kx) & \\
\frac{N^2}{2} \int_0^a (1 - cos2kx)dx &= 1 \\
\text{where } k = \frac{n\pi}{a} & \\
\frac{N^2}{2} \left[a - \int_0^a cos2kxdx \right] &= 1 \\
\text{the integral is zero} & \\
\frac{N^2 a}{2} &= 1 \\
N^2 &= \frac{2}{a}
\end{aligned}$$

We therefore have the normalization constant

$$\boxed{N = \sqrt{\tfrac{2}{a}}} \tag{6.6}$$

Putting it all together, our desired wavefunction is

$$\boxed{\Psi = \sqrt{\tfrac{2}{a}}sinkx} \tag{6.7}$$

Chapter 7

Particle in a 1D Symmetric Box

Picture the following potential with infinite walls like before but centered symmetrically about zero. The potential is described by

- $V = \infty (x \leq \frac{-a}{2})$
- $V = 0 \left(-\frac{a}{2} < x < \frac{a}{2}\right)$
- $V = \infty (x \geq \frac{a}{2})$

The Schrodinger equation is again

$$\boxed{-\frac{\hbar^2}{2m}\frac{d^2\Psi}{dx^2} + V\Psi = \epsilon\Psi} \tag{7.1}$$

This leads to (as done in the previous section)

$$\frac{d^2\Psi}{dx^2} + k^2\Psi = 0$$

where $k = \sqrt{\frac{2m\epsilon}{\hbar^2}}$. The general solutions to this expression are

$$\boxed{\Psi = Ae^{ikx} + Be^{-ikx}} \tag{7.2}$$

Now we must apply our boundary conditions which differ from the previous case

- $\Psi\left(-\frac{a}{2}\right) = 0$

- $\Psi\left(\frac{a}{2}\right) = 0$

Application of the boundary conditions results in the following equations

$$\begin{array}{l} Ae^{-i\frac{ka}{2}} + Be^{i\frac{ka}{2}} = 0 \quad \rightarrow \quad A + Be^{ika} = 0 \\ Ae^{i\frac{ka}{2}} + Be^{-i\frac{ka}{2}} = 0 \quad \rightarrow \quad -A - Be^{-ika} = 0 \end{array}$$

Evaluating these two equations results in

$$\begin{aligned} Be^{ika} - Be^{-ika} &= 0 \\ 2iB\left(\frac{e^{ika} - e^{-ika}}{2i}\right) &= 0 \\ 2iBsinka &= 0 \end{aligned}$$

Energies

So at this point, either $B = 0$ (the trivial solution) or $sinka = 0$. Since we don't want the trivial solution we have

$$\begin{aligned} ka &= n\pi \\ k &= \frac{n\pi}{a} \\ \sqrt{\frac{2m\epsilon}{\hbar^2}} &= \frac{n\pi}{a} \\ \epsilon &= \frac{n^2\pi^2}{a^2}\frac{\hbar^2}{2m} \\ \epsilon &= \frac{n^2h^2}{8ma^2} \end{aligned}$$

We therefore have the desired energies of the system

$$\boxed{\epsilon = \frac{n^2h^2}{8ma^2}} \tag{7.3}$$

Wavefunctions

Now for the wavefunctions. From

$$A + Be^{ika} = 0 \tag{7.4}$$

we get

$$B = -Ae^{-ika}$$

Introduce this expression for B into

$$A + Be^{-ika} = 0$$

to get

$$\begin{aligned} & Ae^{ikx} - Ae^{-ikx}e^{-ika} \\ \Psi = 2iAe^{-i\frac{ka}{2}} & \left(\frac{e^{ikx}e^{i\frac{ka}{2}} - e^{-ikx}e^{-i\frac{ka}{2}}}{2i} \right) \\ \Psi = 2iAe^{-i\frac{ka}{2}} & \left(sink \left(x + \frac{a}{2} \right) \right) \\ \Psi = 2iAe^{-i\frac{ka}{2}} & sin \left[k \left(x + \frac{a}{2} \right) \right] \\ & \text{let } N = 2iAe^{-i\frac{ka}{2}} \\ \Psi = & Nsin \left[k \left(x + \frac{a}{2} \right) \right] \end{aligned}$$

where recall that $k = \dfrac{n\pi}{a}$ and N is our normalization constant.

$$\boxed{\Psi = Nsin \left[k \left(x + \tfrac{a}{2} \right) \right]} \tag{7.5}$$

Now we need to normalize the wavefunction.

$$N^2 \int_{-\frac{a}{2}}^{\frac{a}{2}} sin^2 \left[k \left(x + \frac{a}{2} \right) \right] dx = 1$$

Let $y = (x + \frac{a}{2})$ also $dy = dx$. The limits of integration become

$$\begin{aligned} x &= -\frac{a}{2} \rightarrow y = 0 \\ x &= \frac{a}{2} \rightarrow y = a \end{aligned}$$

We have

$$\begin{aligned}
N^2\int_0^a sin^2 kydy &= 1 \\
\text{where } sin^2 ky = \frac{1}{2}(1-cos2ky) & \\
\frac{N^2}{2}\int_0^a 1-cos2kydy &= 1 \\
\frac{N^2}{2}\left[a-\int_0^a cos2kydy\right] &= 1 \\
\frac{N^2}{2}\left[a-\frac{1}{2k}sin2ky|_0^a\right] &= 1 \\
\text{the second term is zero} & \\
N^2 &= \frac{1}{a}
\end{aligned}$$

Therefore our desired normalization constant is

$$\boxed{N=\sqrt{\tfrac{2}{a}}} \tag{7.6}$$

Putting this all together, our total wavefunction is

$$\boxed{\Psi=\sqrt{\tfrac{2}{a}}sin\left[k\left(x+\tfrac{a}{2}\right)\right]} \tag{7.7}$$

where $k=\frac{n\pi}{a}$

Chapter 8

Alternative particle in a box problems

Picture the following potential. It's the same as the first particle in a box problem. We will solve this problem again but do it slightly differently as you will see. In the end however, the solutions must be the same. Like before the potential goes as

- $V = \infty (x \leq 0)$
- $V = 0 (0 < x < a)$
- $V = \infty (x \geq a)$

The Schrodinger equation is

$$\boxed{-\frac{\hbar^2}{2m}\frac{d^2\Psi}{dx^2} + V\Psi = \epsilon\Psi} \tag{8.1}$$

Rearrange this to get

$$\begin{aligned} -\frac{\hbar^2}{2m}\frac{d^2\Psi}{dx^2} &= \epsilon\Psi \\ \frac{d^2\Psi}{dx^2} &= -\frac{2m\epsilon}{\hbar^2}\Psi \\ \frac{d^2\Psi}{dx^2} + k^2\Psi &= 0 \end{aligned}$$

where as before $k^2 = \frac{2m\epsilon}{\hbar^2}$

Now rather than last time where we assumed a solution of the form $\Psi = Ae^{ikx} + Be^{-ikx}$ we will assume a general solution of the form

$$\boxed{\Psi = Asinkx + Bsinkx} \tag{8.2}$$

Now to get the energies and the particular form of the wavefunction we must apply the boundary conditions intrinsic to the problem.

- $\Psi(0) = 0$
- $\Psi(a) = 0$

If we apply the boundary conditions we get the following from the first boundary condition

$$B = 0$$

Using this and the second boundary condition we learn that

$$Asinka = 0$$

Energies

So again we are left with either the trivial solution ($A = 0$) or that $ka = n\pi$. Working with the desired solution we have

$$\begin{aligned} ka &= n\pi \\ k &= \frac{n\pi}{a} \\ \text{where } k = \sqrt{\frac{sm\epsilon}{\hbar^2}} & \\ \sqrt{\frac{2m\epsilon}{\hbar^2}} &= \frac{n\pi}{a} \\ \epsilon &= \frac{n\pi^2}{a^2}\frac{\hbar^2}{2m} \\ \epsilon &= \frac{n^2h^2}{8ma^2} \end{aligned}$$

The desired energies of the particle in a box are therefore

$$\boxed{\epsilon = \tfrac{n^2h^2}{8ma^2}} \tag{8.3}$$

Wavefunctions

Since $\Psi = Asinkx$ we must now normalize the wavefunction.

$$\begin{aligned} A^2 \int_0^a sin^2 kx dx &= 1 \\ \text{where } sin^2 kx &= \frac{1}{2}(1 - cos2kx) \\ \frac{A^2}{2}\left[\int_0^a 1 - cos2kxdx\right] &= 1 \\ \frac{A^2}{2}\left[a - \frac{1}{2k} sin2kx|_0^a\right] &= 1 \\ \frac{A^2 a}{2} &= 1 \\ A^2 &= \frac{2}{a} \end{aligned}$$

leaving us with the desired normalization constant

$$\boxed{A = \sqrt{\tfrac{2}{a}}} \tag{8.4}$$

The total wavefunction is then

$$\boxed{\Psi = \sqrt{\tfrac{2}{a}} sinkx} \tag{8.5}$$

which is identical to the expression we had previously.

Probability densities

Example

What is the probability P of locating an electron between $x = 0$ and $x = 0.2nm$ in the ground state of a 1D box of length 1.0 nm? Use the previously derived particle in a box solutions.

$$P = \int_0^{0.2} (\text{Probability density}) dx$$

where (Probability density) $= \Psi^*\Psi = \frac{2}{a}sin^2kx$ and where $a = 1$ nm.

$$\begin{aligned}
P &= \int_0^a \frac{2}{L}sin^2kxdx \\
&= \frac{2}{L}\frac{1}{2}\int_0^a 1 - cos^2 2kxdx \\
&= \frac{1}{L}\left[a - \frac{1}{2k}sin2kx|_0^a\right] \\
&= \frac{1}{L}\left[a - \frac{1}{2k}\left(sin2ka\right)\right] \\
&\quad \text{where } k = \frac{n\pi}{L} \text{ and } n = 1
\end{aligned}$$

resulting in

$$\boxed{P = \frac{1}{L}\left[a - \frac{1}{2k}sin\left(\frac{2\pi a}{L}\right)\right]} \tag{8.6}$$

Can leave the expression like this if desired. Plugging in the relevant values for k, L and a we have

$$\begin{aligned}
P &= \frac{1}{1.0nm}\left[0.2nm - \frac{1.0nm}{2\pi}sin\left(2\pi\frac{0.2}{1.0}\right)\right] \\
&= \frac{1}{1.0nm}\left[0.2nm - \frac{1}{2\pi}\left(0.9511\right)\right] \\
&= 0.0486 \\
&\simeq 0.05
\end{aligned}$$

The desired probability of finding the particle in the specified interval is approximately 5%.

Expectation values

Example 1

What is the average position, x, of a particle in a box?

Recall that to find expectation values you must sandwich the operator.

$$< x >= \int_0^a \Psi^* x \Psi dx$$

where recall that we found earlier that $\Psi = \sqrt{\frac{2}{a}}sinkx$. This leaves us with

$$\begin{aligned}
< x > &= \int_0^a \left(\sqrt{\frac{2}{a}} sinkx\right)(x)\left(\sqrt{\frac{2}{a}} sinkx\right) dx \\
& \text{where we recall that the complex conjugate} \\
& \text{of a real wavefunction is itself.} \\
&= \int_0^a \frac{2}{a} x sin^2 kx dx \\
&= \frac{1}{a}\int_0^a x sin^2 kx dx \\
& \text{where } sin^2 kx = \frac{1}{2}(1 - cos 2kx) \\
&= \frac{1}{a}\frac{2}{a}\int_0^a x(1 - cos 2kx)dx \\
&= \frac{1}{a}\left[\frac{x^2}{2}|_0^a - \int_0^a x cos 2kx dx\right] \\
&= \frac{a}{2} - \frac{1}{a}\int_0^a x cos 2kx dx
\end{aligned}$$

We integrate the second term by parts. Let $u = x$, $du = dx$. Let $dv = cos2kxdx$ and therefore $v = \frac{1}{2k} sin2kx$. The integral becomes

$$\int_0^a x cos 2kx dx = \left[\frac{x}{2k} sin 2kx|_0^a - \int_0^a \frac{1}{2k} sin 2kx dx\right]$$

Since $k = \frac{n\pi}{a}$ the first term is zero. We now have

$$\begin{aligned}
< x > &= \frac{a}{2} - \frac{1}{2ka}\int_0^a sin 2kx dx \\
&= \frac{a}{2} + \frac{1}{2ka}\left(\frac{1}{2k}\right) cos 2kx|_0^a \\
&= \frac{a}{2} + \frac{1}{4k^2 a}\left[cos \frac{2n\pi}{a} a - 1\right] \\
&= \frac{a}{2}
\end{aligned}$$

We are therefore left with our final result

$$\boxed{< x >= \frac{a}{2}} \tag{8.7}$$

The average position of the particle in a box is the midpoint.

Example 2

What is the average momentum p of a particle in a box of width a.

Recall that one must sandwich the operator.

$$\begin{aligned}
<p> &= \int_0^a \Psi^* p \Psi dx \\
&= \int_0^a \Psi^* \left(-i\hbar \frac{d}{dx}\right) \Psi dx \\
&\quad \text{where recall again that } \Psi = \sqrt{\frac{2}{a}} sinkx \\
&\quad \text{and that the complex conjugate of} \\
&\quad \text{something real stays real.}
\end{aligned}$$

We have

$$\begin{aligned}
<p> &= -\frac{2}{a}\int_0^a i\hbar k sinkx coskx dx \\
&= -\frac{2i\hbar k}{a}\int_0^a sinkx coskx dx \\
&\quad \text{and where recall } \frac{1}{2} sin2kx = sinkx coskx \\
&= -\frac{i\hbar k}{a}\int_0^a sin2kx dx \\
&= \frac{i\hbar k}{a}\left(\frac{1}{2k}\right) cos2kx|_0^a \\
&= \frac{i\hbar}{2a}(cos2ka - 1) = 0
\end{aligned}$$

The term in parenthesis is zero since $k = \frac{n\pi}{a}$ We are left with

$$\boxed{<p>= 0} \qquad (8.8)$$

The average momentum of a particle in a box is zero.

Chapter 9

Particle in an infinite 3D box

Basics

Here we illustrate the concept of a “separable” Hamiltonian. The particle in a 3D infinte box is basically an extension of the particle in a 1D box problem three times over. The relevant potential is

- $V = 0$ if $(0 < x < a)$
- and if $(0 < x < b)$
- and if $0(< x < c)$

otherwise the potential is infinite.

Here the Schrodinger equation that we need to solve looks like

$$\begin{aligned} -\frac{\hbar^2\nabla^2}{2m}\Psi + V\Psi &= \epsilon\Psi \\ \text{where } V = 0 & \\ -\frac{\hbar^2\nabla^2}{2m}\Psi &= \epsilon\Psi \end{aligned}$$

where in Cartesian coordinates the Laplacian (∇^2 or Δ) is $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$. We have

$$\boxed{-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\Psi = \epsilon\Psi} \tag{9.1}$$

Now note that we can see that the Hamiltonian operator can be written as a sum of distinct x, y, and z components.

$$H = H_x + H_y + H_z$$

where

$$\begin{aligned} H_x &= -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} \\ H_y &= -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial y^2} \\ H_z &= -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial z^2} \end{aligned}$$

This means that the Hamiltonian is “separable”. As a consequence the eigenfunction of the entire system is the product of the individual eigenfunctions if x, y, and z components were considered separately. Furthermore, the eigenvalue of the system is the sum of individual eigenvalues if x, y, and z components were considered separately.

$$\begin{aligned} \Psi_{tot} &= \Psi_x\Psi_y\Psi_z \\ \epsilon_{tot} &= \epsilon_x + \epsilon_y + \epsilon_z \end{aligned}$$

All this means for you and me is that all we have to do is solve 3 individual particle in a box problems, add the energies to get the total energy and multiply the wavefunctions to get the total wavefunction. We have

$$-\frac{\hbar^2}{2m}\frac{d^2\Psi_x}{dx^2} = \epsilon_x\Psi_x$$
$$-\frac{\hbar^2}{2m}\frac{d^2\Psi_y}{dy^2} = \epsilon_y\Psi_y$$
$$-\frac{\hbar^2}{2m}\frac{d^2\Psi_z}{dz^2} = \epsilon_z\Psi_z$$

We know from before that the individual solutions are

$$\Psi_x = \sqrt{\frac{2}{a}} sink_x x$$
$$\Psi_y = \sqrt{\frac{2}{b}} sink_y y$$
$$\Psi_z = \sqrt{\frac{2}{c}} sink_z z$$

where $k_x = \frac{n_x\pi}{a}$, $k_y = \frac{n_y\pi}{b}$ and $k_z = \frac{n_z\pi}{c}$.

We also know that the energies are

$$\epsilon_x = \frac{n_x^2 h^2}{8ma^2}$$
$$\epsilon_y = \frac{n_y^2 h^2}{8mb^2}$$
$$\epsilon_z = \frac{n_z^2 h^2}{8mc^2}$$

where $n_x = 1, 2, 3 \ldots$, $n_y = 1, 2, 3 \ldots$, and $n_z = 1, 2, 3 \ldots$.

Summary

Putting everything together we have

$$\boxed{\Psi_{tot} = \Psi_x \Psi_y \Psi_z = \sqrt{\tfrac{8}{abc}} sink_x x sink_y y sink_z z} \tag{9.2}$$

and

$$\boxed{\epsilon_{tot} = \tfrac{h^2}{8m}\left(\tfrac{n_x^2}{a^2} + \tfrac{n_y^2}{b^2} + \tfrac{n_z^2}{c^2}\right)} \tag{9.3}$$

Note that it takes 3 quantum numbers (n_x, n_y, n_z) to specify the system.

Expectation values

Like before we can find the average value of the position $(< r >)$ and the average value of the momentum $< p >$ for the particle in a 3D box.

Example 1

Let's do the average position first. Any thoughts as to what the outcome must be?

$$\boxed{< r >= \textstyle\int \Psi^*(x, y, z)\hat{r}\Psi(x, y, z)dxdydz} \tag{9.4}$$

where $\hat{r} = \hat{x}i + \hat{y}j + \hat{z}k$

Let's look at the x component $(< x >)$ first.

$$\begin{aligned} < x > &= \int \left(\sqrt{\frac{2}{a}} sink_x x \sqrt{\frac{2}{b}} sink_y y \sqrt{\frac{2}{c}} sink_z z\right) x \left(\sqrt{\frac{2}{a}} sink_x x \sqrt{\frac{2}{b}} sink_y y \sqrt{\frac{2}{c}} sink_z z\right) dxdydz \\ &= \int_0^b \frac{2}{b} sin^2 k_y y dy \int_0^c \frac{2}{c} sin^2 k_z z dz \int_0^a x \frac{2}{a} sin^2 k_x x dx \end{aligned}$$

Now by normalization, the first two integrals equal 1. We can prove it if you want

$$\begin{aligned}\frac{2}{b}\int_0^b sin^2k_y y dy &= \frac{2}{b}\frac{1}{2}\int_0^b 1-cos2k_y y dy\\ &= \frac{1}{b}\left[b-\frac{1}{2k_y}\;sin2k_y y|_0^b\right]\\ &= 1\end{aligned}$$

Having showed this we have

$$<x>=\frac{2}{a}\int_0^a x sin^2k_x x dx$$

which we have evaluated previously. Note that $sin^2k_x x=\frac{1}{2}(1-cos2k_x x)$ giving

$$\begin{aligned}<x> &= \frac{1}{a}\int_0^a x - x cos2k_x x dx\\ &= \frac{1}{a}\left[\frac{x^2}{2}\bigg|_0^a - \int_0^a x cos2k_x x dx\right]\\ &= \frac{1}{a}\left[\frac{a^2}{2}-\int_0^a x cos2k_x x dx\right]\\ &= \frac{a}{2}-\frac{1}{a}\int_0^a x cos2k_x x dx\end{aligned}$$

Integrate this last expression by parts where $u=x$, $du=dx$, $dv=cos2k_x x dx$ and $v=\frac{1}{2k_x}sin2k_x x$. We have

$$\begin{aligned}<x> &= \frac{a}{2}-\frac{1}{a}\left[\frac{x}{2k_x}sin2k_x x\bigg|_0^a-\frac{1}{2k_x}\int_0^a sin2k_x x dx\right]\\ &= \frac{a}{2}-\frac{1}{2k_x a}\left(\frac{1}{2k_x}\right)cos2k_x x\;|_0^a\\ &= \frac{a}{2}-\frac{1}{4k_x^2 a}(cos2k_x a-1)\\ &= \frac{a}{2}\end{aligned}$$

therefore

$$\boxed{<x>=\frac{a}{2}} \tag{9.5}$$

By the same token it can be shown that

$$\boxed{< y >= \tfrac{b}{2}} \tag{9.6}$$

$$\boxed{< z >= \tfrac{c}{2}} \tag{9.7}$$

Summarizing we then have

$$\boxed{< r >= \tfrac{a}{2}i + \tfrac{b}{2}j + \tfrac{c}{2}k} \tag{9.8}$$

which is the exact center of the cube.

Example 2

We can also find the average momentum $< p >$ of the particle in a 3D box

$$\boxed{< p >= \int \Psi^*(x,y,z)\hat{p}\Psi(x,y,z)dxdydz} \tag{9.9}$$

where $\hat{p} = -i\hbar\nabla$ or $\hat{p} = -i\hbar\left(i\frac{\partial}{\partial x} + j\frac{\partial}{\partial y} + k\frac{\partial}{\partial z}\right)$.

Like the previous example, we can just do p_x and the rest will follow.

$$\begin{aligned} < p_x > &= \int \left(\sqrt{\frac{2}{a}}sink_xx\sqrt{\frac{2}{b}}sink_yy\sqrt{\frac{2}{c}}sink_zz\right) - i\hbar\frac{\partial}{\partial x}\left(\sqrt{\frac{2}{a}}sink_xx\sqrt{\frac{2}{b}}sink_yy\sqrt{\frac{2}{c}}sink_zz\right)dxdydz \\ &= \int_0^b \left(\frac{2}{b}\right) sin^2k_yydy \int_0^c \left(\frac{2}{c}\right) sin^2k_zzdz \int_0^a \left(\frac{2}{a}\right) sink_xx(-i\hbar)cosk_xxdx \end{aligned}$$

The first two integrals are equal to 1 by nomalization leaving

$$< p_x >= -\frac{2i\hbar}{a}\int_0^a sink_xxcosk_xxdx$$

where $\frac{1}{2}sin2k_xx = sink_xxcosk_xx$

$$\begin{aligned} < p_x > &= -\frac{i\hbar}{a}\int_0^a sin2k_xxdx \\ &= \frac{i\hbar}{a}\left(\frac{1}{2k_x}\right) cos2k_xx|_0^a \\ &= \frac{i\hbar}{2k_xa}(cos2k_xa - 1) \\ &= 0 \end{aligned}$$

Therefore

$$\boxed{< p_x >= 0} \tag{9.10}$$

By the same token

$$\boxed{< p_y >= 0} \tag{9.11}$$

$$\boxed{< p_z >= 0} \tag{9.12}$$

and $< p >=< p_x > i+ < p_y > j+ < p_z > k$ resulting in

$$\boxed{< p >= 0} \tag{9.13}$$

The average momentum of a particle in a 3D box is zero.

Degeneracy

Assume as we have above that the lengths of the box are all the same $a = b = c$ what are the "degeneracies" of the different energy levels?

Recall that

$$\epsilon_{tot} = \frac{h^2}{8ma^2}(n_x^2 + n_y^2 + n_z^2)$$

where $n_x = 1, 2, 3 \ldots$, $n_y = 1, 2, 3 \ldots$, and $n_z = 1, 2, 3 \ldots$ and that the state of the system is defined by these three quantum numbers.

The lowest energy state is

- (1,1,1)

This state is "non-degenerate"

The next lowest energy state is

- (1,2,1)
- (1,1,2)
- (2,1,1)

Since there are 3 states with the same energy, this state is threefold degenerate.

The next lowest energy state is

- (1,2,2)

- (2,1,2)
- (2,2,1)

This state is also threefold degenerate.

The next lowest energy state is

- (3,1,1)
- (1,3,1)
- (1,1,3)

Again, this state is threefold degenerate

The next lowest energy is

- (2,2,2)

This state like the lowest energy state is non-degenerate.

So you can gather from the above examples that by "degenerate" we mean that there are multiple states with the same energy. This degeneracy arises due to the symmetry of the cube. In the above example, the degeneracy can be lifted if the box is stretched along one or more directions in order to break the symmetry of the problem.

Breaking the symmetry of the problem

For example, let $c \neq b = a$ and in particular let $c = 2a$. For the energies we have the following expression

$$\begin{aligned}\epsilon_{tot} &= \frac{h^2}{8m}\left(\frac{n_x^2 + n_y^2}{a^2} + \frac{n_z^2}{4a^2}\right) \\ &= \frac{h^2}{8ma^2}\left(n_x^2 + n_y^2 + \frac{1}{4}n_z^2\right)\end{aligned}$$

The states and their degeneracies in increasing order of energy are

- (1,1,1) nondegenerate
- (1,1,2) nondegenerate
- (1,1,3) nondegenerate
- (2,1,1),(1,2,1) 2-fold degenerate

- (1,1,4) nondegenerate
- (1,1,5), (2,2,1) 2-fold degenerate
- (1,3,1),(3,1,1) 2-fold degenerate
- (1,1,6) nondegenerate
- etc…

You can see that there are a fewer number of degenerate states. Breaking the symmetry of the problems lifts these degeneracies.

Chapter 10

Particle in a sphere

This is a more complicated problem. Two approaches to a solution are illustrated with one leading to what are know as spherical Bessel function and the other to a solution involving regular Bessel functions of half integer order. The Schrodinger equation is

$$\boxed{-\tfrac{\hbar^2}{2m}\nabla^2\Psi + V\Psi = \varepsilon\Psi}$$

The potential is

$$\begin{aligned} V(r) &= 0 \text{ if } r < a \\ V(r) &= \infty \text{ if } r \geq a \end{aligned}$$

In the region inside the sphere where $V = 0$, this reduces to

$$-\frac{\hbar^2}{2m}\nabla^2\Psi = \varepsilon\Psi \tag{10.1}$$

where

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2 sin(\theta)}\frac{\partial}{\partial\theta}\left(sin(\theta)\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2(\theta)}\frac{\partial^2}{\partial\phi^2} \tag{10.2}$$

If replaced into the above equation, multiply by $2mr^2$ on both sides to simplify giving

$$-\hbar^2 r^2\nabla^2\Psi = 2mr^2\varepsilon\Psi$$

Expanded out this looks like

$$-\hbar^2 r^2\left(\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\Psi}{\partial r}\right)+\frac{1}{r^2 sin(\theta)}\frac{\partial}{\partial\theta}\left(sin(\theta)\frac{\partial\Psi}{\partial\theta}\right)+\frac{1}{r^2\sin^2(\theta)}\frac{\partial^2\Psi}{\partial\phi^2}\right)$$
$$=2mr^2\varepsilon\Psi$$

$$-\hbar^2\left(\frac{\partial}{\partial r}\left(r^2\frac{\partial\Psi}{\partial r}\right)+\frac{1}{sin(\theta)}\frac{\partial}{\partial\theta}\left(sin(\theta)\frac{\partial\Psi}{\partial\theta}\right)+\frac{1}{sin^2(\theta)}\frac{\partial^2\Psi}{\partial\phi^2}\right)$$
$$=2mr^2\varepsilon\Psi$$

Rearrange to give

$$\begin{aligned}-\quad&\hbar^2\frac{\partial}{\partial r}\left(r^2\frac{\partial\Psi}{\partial r}\right)-2mr^2\varepsilon\Psi\\-\quad&\hbar^2\left(\frac{1}{sin(\theta)}\frac{\partial}{\partial\theta}\left(sin(\theta)\frac{\partial}{\partial\theta}\right)-\frac{1}{sin^2(\theta)}\frac{\partial^2}{\partial\phi^2}\right)\Psi=0\end{aligned}$$

where recall that the third term looks familiar. Basically

$$\hat{L}^2=-\hbar^2\left(\frac{1}{sin(\theta)}\frac{\partial}{\partial\theta}\left(sin(\theta)\frac{\partial}{\partial\theta}\right)-\frac{1}{sin^2(\theta)}\frac{\partial^2}{\partial\phi^2}\right)\tag{10.3}$$

(Angular momentum operator). Our main equation then becomes

$$-\hbar^2\frac{\partial}{\partial r}\left(r^2\frac{\partial\Psi}{\partial r}\right)-2mr^2\varepsilon\Psi+\hat{L}^2\Psi=0$$

Furthermore, recall that $\hat{L}^2\Psi=\hbar^2 l(l+1)\Psi$ (angular momentum eigenvalues) leading to

$$-\hbar^2\frac{\partial}{\partial r}\left(r^2\frac{\partial\Psi}{\partial r}\right)-2mr^2\varepsilon\Psi+\hbar^2 l(l+1)\Psi=0$$

Simplify this

$$\begin{aligned}-\hbar^2\quad&\frac{\partial}{\partial r}\left(r^2\frac{\partial\Psi}{\partial r}\right)-\Psi\left(2mr^2\varepsilon-\hbar^2 l(l+1)\right)=0\\&\frac{\partial}{\partial r}\left(r^2\frac{\partial\Psi}{\partial r}\right)+\Psi\left(\frac{2m\varepsilon}{\hbar^2}r^2-l(l+1)\right)=0\end{aligned}$$

Let $k^2=\frac{2m\varepsilon}{\hbar^2}$ giving

$$\frac{\partial}{\partial r}\left(r^2\frac{\partial\Psi}{\partial r}\right)+\Psi\left(k^2r^2-l(l+1)\right)=0\tag{10.4}$$

At this point there are two ways to proceed from this equation. The first will lead to solutions involving so called "spherical" Bessel functions. The other will lead to solutions involving regular or normal Bessel functions of half integer order. Spherical and half integer order, normal, Bessel functions are proportional to each other so ultimately the solutions are the same.

Solution with spherical Bessel functions

Let $\Psi = x(r)y(\theta,\phi)$ The we can evaluate the following items using x and y as shorthand for $x(r)$ and $y(\theta,\phi)$

- $\frac{\partial \Psi}{\partial r} = yx^{'}$
- $r^2\frac{\partial \Psi}{\partial r} = yr^2x^{'}$
- $\frac{\partial}{\partial r}\left(r^2\frac{\partial \Psi}{\partial r}\right) = y(r^2x^{''} + 2rx^{'})$

Replace the last item into equation 23 giving

$$y(r^2x^{''} + 2rx^{'}) + xy(k^2r^2 - l(l+1)) = 0$$

Divide out y and continue simplifying.

$$r^2x^{''} + 2rx^{'} + x(k^2r^2 - l(l+1)) = 0$$

Let $z = kr$ (therefore $dr = \frac{dz}{k}$ and $dr^2 = \frac{dz^2}{k^2}$. these will be useful in a moment) and replace into the above expression

$$\begin{aligned} r^2x^{''} + 2rx^{'} + x(z^2 - l(l+1)) &= 0 \\ r^2\frac{d^2x}{dr^2} + 2r\frac{dx}{dr} + x(z^2 - l(l+1)) &= 0 \\ k^2r^2\frac{d^2x}{dz^2} + 2rk\frac{dx}{dz} + x(z^2 - l(l+1)) &= 0 \end{aligned}$$

or

$$\boxed{z^2\frac{d^2x}{dz^2} + 2z\frac{dx}{dz} + x(z^2 - l(l+1)) = 0} \tag{10.5}$$

This is the general spherical Bessel equation whose solutions take the form:

$$\boxed{x(r) = Aj_l(z) + By_l(z)} \tag{10.6}$$

where $j_l(z)$ are spherical Bessel functions of the first kind and $y_l(z)$ are spherical Bessel functions of the second kind (also known as spherical Neumann functions written as $n_l(z)$). Note that $j_l(z)$ is finite and well behaved at the origin while $y_l(z)$ diverges. So to get a physical solution, one must drop the spherical Bessel functions of the second kind leaving

$$\boxed{x(r) = Aj_l(z)} \tag{10.7}$$

The equation and its solutions can be looked up in a text like "Handbook of Mathematical Functions" Abramowitz and Stegun, pg 437. Note that these spherical Bessel functions are denoted by little $j_n(z)$ as opposed to big $J_n(z)$ which are normal Bessel functions (same with spherical Bessel functions of the second kind). Furthermore, spherical bessel functions are related to half integer Bessel functions, a subclass of normal Bessel functions as shown at the end of this chapter. Examples of the spherical Bessel function solutions are

- $j_0(z) = \frac{sin(z)}{z}$
- $j_1(z) = \frac{sin(z)}{z^2} - \frac{cos(z)}{z}$
- $j_2(z) = 3\frac{sin(z)}{z^3} - 3\frac{cos(z)}{z^2} - \frac{sin(z)}{z}$

and so forth.

Solution with half integer (normal) Bessel functions

Alternatively assume that the wavefunction has the form $\psi = \frac{x(r)}{r}y(\theta, \phi) = R(r)y(\theta, \phi)$ Replace this in equation 24 and start simplifying.

$$\frac{\partial}{\partial r}\left(r^2\frac{\partial\Psi}{\partial r}\right) + \Psi(k^2r^2 - l(l+1)) = 0$$

We need the following bits of information

- $\frac{\partial\Psi}{\partial r} = yx\left(-\frac{1}{r^2}\right) + \frac{y}{r}x'$
- $r^2\frac{\partial\Psi}{\partial r} = -xy + ryx'$
- $\frac{\partial}{\partial r}\left(r^2\frac{\partial\Psi}{\partial r}\right) = -x'y + x''ry + x'y = x''ry$

Replace the last item into our main equation

$$x^{''}ry + \frac{xy}{r}(k^2r^2 - l(l+1)) = 0$$

Get rid of y

$$rx^{''} + \frac{x}{r}(k^2r^2 - l(l+1)) = 0$$

$$x^{''} + x\left(k^2 - \frac{l(l+1)}{r^2}\right) = 0$$

Now let $z = kr$ and $x = \sqrt{z}\phi(z)$ $\left(dr = \frac{dz}{k}\right)$ giving

$$\frac{d^2x}{dr^2} + x\left(k^2 - \frac{l(l+1)}{r^2}\right) = 0$$

$$k^2\frac{d^2x}{dz^2} + \sqrt{z}\phi\left(k^2 - \frac{k^2l(l+1)}{z^2}\right) = 0$$

Use the following bits of information

- $\frac{dx}{dz} = \sqrt{z}\phi^{'} + \phi\frac{1}{2}z^{-\frac{1}{2}}$
- $\frac{d^2x}{dz^2} = \sqrt{z}\phi^{''} + \phi^{'}\frac{1}{2}z^{-\frac{1}{2}} + \frac{1}{2}\left(\phi\left(-\frac{1}{2}\right)z^{-\frac{3}{2}} + z^{-\frac{1}{2}}\phi^{'}\right)$
- $\frac{d^2x}{dz^2} = \sqrt{z}\phi^{''} + \phi^{'}z^{-\frac{1}{2}} - \frac{1}{4}\phi z^{-\frac{3}{2}}$

especially the last term to get

$$k^2\left(\sqrt{z}\phi^{''} + \phi^{'}z^{-\frac{1}{2}} - \frac{\phi}{4}z^{-\frac{3}{2}}\right) + \sqrt{z}\phi\left(k^2 - \frac{k^2l(l+1)}{z^2}\right) = 0$$

Drop k^2 and continue simplifying

$$\sqrt{z}\phi^{''} + \phi^{'}z^{-\frac{1}{2}} - \frac{\phi}{4}z^{-\frac{3}{2}} + \sqrt{z}\phi\left(1 - \frac{l(l+1)}{z^2}\right) = 0$$

$$z\phi^{''} + \phi^{'} - \frac{\phi}{4z} + z\phi\left(1 - \frac{l(l+1)}{z^2}\right) = 0$$

$$z^2\phi^{''} + z\phi^{'} - \frac{\phi}{4} + z^2\phi\left(1 - \frac{l(l+1)}{z^2}\right) = 0$$

$$z^2\phi^{''} + z\phi^{'} + \phi\left(-\frac{1}{4} + z^2 - l(l+1)\right) = 0$$

$$z^2\phi^{''} + z\phi^{'} + \phi\left(z^2 - \left(\frac{1}{4} + l(l+1)\right)\right) = 0$$

Note that the term in the inner parenthesis is equal to $\left(l+\frac{1}{2}\right)^2$ This simplifies the full expression to

$$z^2\phi^{''}+z\phi^{'}+\phi\left(z^2-\left(l+\frac{1}{2}\right)^2\right)=0$$

Let $n=\left(l+\frac{1}{2}\right)$

$$\boxed{z^2\phi^{''}+z\phi^{'}+\phi(z^2-n^2)=0} \tag{10.8}$$

This is the normal Bessel function equation. In this case where we have half-integer orders n then general solutions for ϕ are linear combinations of half integer Bessel functions. Furthermore, since $x(r)=\sqrt{z}\phi(z)$ and $R(r)=\frac{x(r)}{r}$ the general radial solution, $R(r)$, is

$$\begin{aligned}\phi(z) &= AJ_n(z)+BJ_n(z)\\ x(r) &= \sqrt{z}\left(A^{'}J_n(z)+B^{'}Y_n(z)\right)\end{aligned}$$

$$\boxed{R(r)=\frac{1}{\sqrt{z}}\left(A^{'}J_n(z)+B^{'}Y_n(z)\right)} \tag{10.9}$$

or more explicitly

$$\boxed{x(r)=\sqrt{z}\left(AJ_{\left(l+\frac{1}{2}\right)}(z)+BY_{\left(l+\frac{1}{2}\right)}(z)\right)} \tag{10.10}$$

We can look up the equation and its solution in a book like Abramowitz and Stegun but since Y_n diverges near the origin so it should be dropped immediately. This leaves

$$\boxed{R(r)=\frac{A^{'}}{\sqrt{z}}J_{\left(l+\frac{1}{2}\right)}(z)} \tag{10.11}$$

Summary

So in the end, regardless of how you came to the solution, to find the eignevalues we need to find the roots, α, of either

$$\boxed{j_l(kr)=0}\ \text{spherical Bessel} \tag{10.12}$$

$$\boxed{J_{\left(l+\frac{1}{2}\right)}(kr)=0}\ \text{half integer Bessel} \tag{10.13}$$

So on finding the root one also has $\alpha = kr$ and from this the desired value of k. Note that for each value of l there are an infinite number of roots. The eigenvalues are then

$$\begin{aligned} ka &= \alpha \\ \sqrt{\frac{2m\varepsilon}{\hbar^2}}a &= \alpha \\ \varepsilon &= \frac{\hbar^2\alpha^2}{2ma^2} \end{aligned}$$

leading to

$$\varepsilon = \frac{\hbar^2 k^2}{2m}$$

$$\boxed{\varepsilon = \frac{\hbar^2\alpha^2}{2ma^2}} \tag{10.14}$$

Finally, the relation between spherical Bessel functions and half integer Bessel functions are:

$$j_l(z) = \sqrt{\frac{\pi}{2z}}J_{(l+\frac{1}{2})}(z) \tag{10.15}$$

$$y_l = n_l(z) = \sqrt{\frac{\pi}{2z}}Y_{(l+\frac{1}{2})}(z) \tag{10.16}$$

So either approach to solving the problem is valid. Its your choice on what's most convenient.

Chapter 11

Harmonic Oscillator: Analytical approach

Start with the time independent Schrodinger equation

$$H\Psi = \epsilon\Psi$$

where $H = -\frac{\hbar^2\nabla^2}{2m} + V(r)$. For simplicity consider only a 1D problem. We have on rearranging the Schrodinger equation.

$$\begin{aligned}
\left(-\frac{\hbar^2\nabla^2}{2m} + V\right)\Psi &= \epsilon\Psi \\
\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V\right)\Psi &= \epsilon\Psi \\
\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V - \epsilon\right)\Psi &= 0 \\
\left(\frac{d^2}{dx^2} - \frac{2m}{\hbar^2}(V-\epsilon)\right)\Psi &= 0 \\
\left(\frac{d^2}{dx^2} + \frac{2m}{\hbar^2}(\epsilon-V)\right)\Psi &= 0
\end{aligned}$$

Now to continue simplifying things let

- $x = \alpha y$ where α has units of distance
- $\epsilon = \beta\varepsilon$ where β has units of energy
- $V = \frac{1}{2}m\omega x^2$ where $\omega = \sqrt{\frac{k}{m}}$

- k is a force constant, m is the particle mass
- $\frac{d^2}{dx^2} \to \frac{1}{\alpha^2}\frac{d^2}{dy^2}$

Putting everything together we have

$$\begin{aligned}
\left(\frac{1}{\alpha^2}\frac{d^2}{dy^2}+\frac{2m}{\hbar^2}(\beta\varepsilon-\frac{1}{2}m\omega^2x^2)\right)\Psi &= 0\\
\left[\frac{1}{\alpha^2}\frac{d^2}{dy^2}+\frac{2m}{\hbar^2}(\beta\varepsilon-\frac{m\omega^2\alpha^2y^2}{2})\right]\Psi &= 0\\
\left[\frac{d^2}{dy^2}+\frac{2m\alpha^2}{\hbar^2}(\beta\varepsilon-\frac{m\omega^2\alpha^2y^2}{2})\right]\Psi &= 0\\
\left[\frac{d^2}{dy^2}+\frac{2m\alpha^2\beta\varepsilon}{\hbar^2}-\frac{m^2\omega^2\alpha^4y^2}{\hbar^2}\right]\Psi &= 0
\end{aligned}$$

Define α and β now such that

$$\boxed{\frac{2m\beta\alpha^2}{\hbar^2}=1} \tag{11.1}$$

$$\boxed{\frac{m^2\omega^2\alpha^4}{\hbar^2}=1} \tag{11.2}$$

When you make these changes the equation we obtain is

$$\boxed{\left[\frac{d^2}{dy^2}+\varepsilon-y^2\right]\Psi=0} \tag{11.3}$$

This is the equation that we will solve.

Brief aside, units

First evaluate α

$$\begin{aligned}
\frac{m^2\omega^2\alpha^4}{\hbar^2} &= 1\\
\alpha^4 &= \frac{\hbar^2}{m^2\omega^2}\\
\alpha^2 &= \frac{\hbar}{m\omega}
\end{aligned}$$

leading to

$$\boxed{\alpha=\sqrt{\frac{\hbar}{m\omega}}} \tag{11.4}$$

So now what are the units of α?

- $\hbar \to j \cdot s$
- $m \to kg$
- $\omega \to s^{-1}$

From this you find that α has units of length. This is the natural lengthscale of our problem.

Next for β

$$\begin{aligned} \frac{2m\beta\alpha^2}{\hbar^2} &= 1 \\ \frac{2m\beta}{\hbar^2}\frac{\hbar}{m\omega} &= 1 \\ \frac{2\beta}{\hbar\omega} &= 1 \end{aligned}$$

leading to

$$\boxed{\beta = \tfrac{\hbar\omega}{2}} \tag{11.5}$$

Now what are the units of β?

- $\hbar \to j \cdot s$
- $\omega \to s^{-1}$

From this you find that β has units of energy. This is the natural energy scale of the problem.

Now back to our original problem. We left off with

$$\left(\frac{d^2}{dy^2} + (\varepsilon - y^2)\right)\Psi = 0$$

Try a general solution to this equation of the form

$$\boxed{\Psi(y) = f(y)e^{-\frac{y^2}{2}}} \tag{11.6}$$

where it will ultimately be seen that $f(y)$ are Hermite polynomials.

Let's plug this general solution into our above expression and see what we get. Looking ahead we will need to evaluate some second derivatives. Let's do this here ahead of time.

First derivative

$$\begin{aligned}\frac{d}{dy}[f(y)e^{-\frac{y^2}{2}}] &= f(y)(-\frac{1}{2})(2y)e^{-\frac{y^2}{2}} + f^{'}(y)e^{-\frac{y^2}{2}} \\ &= -f(y)ye^{-\frac{y^2}{2}} + f^{'}(y)e^{-\frac{y^2}{2}}\end{aligned}$$

The first derivative is therefore

$$\frac{d\Psi(y)}{dy} = [-yf(y) + f^{'}(y)]e^{-\frac{y^2}{2}} \tag{11.7}$$

Second derivative

Now go and find the second derivative.

$$\begin{aligned}\frac{d\Psi(y)}{dy} &= [-yf(y) + f^{'}(y)]e^{-\frac{y^2}{2}}(-\frac{1}{2})(2y) + [-yf^{'}(y) - f(y) + f^{''}(y)]e^{-\frac{y^2}{2}} \\ &= [y^2 f(y) - yf^{'}(y)]e^{-\frac{y^2}{2}} + [-yf^{'}(y) - f(y) + f^{''}(y)]e^{-\frac{y^2}{2}}\end{aligned}$$

yielding our desired second derivative

$$\boxed{\frac{d^2\Psi(y)}{dy^2} = [f^{''}(y) - 2yf^{'}(y) + (y^2-1)]e^{-\frac{y^2}{2}}} \tag{11.8}$$

Now back to our original expression.

$$\begin{aligned}\frac{d^2\Psi}{dy^2} + (\varepsilon - y^2)\Psi &= 0 \\ \left[f^{''}(y) - 2yf^{'}(y) + (y^2-1)f(y)\right]e^{-\frac{y^2}{2}} + (\varepsilon - y^2)f(y)e^{-\frac{y^2}{2}} &= 0 \\ f^{''}(y) - 2yf^{'}(y) + (y^2-1)f(y) + (\varepsilon - y^2)f(y) &= 0 \\ f^{''}(y) - 2yf^{'}(y) - f(y) + \varepsilon f(y) &= 0 \\ f^{''} - 2yf^{'}(y) + (\varepsilon - 1)f(y) &= 0 \\ \text{now define } (\varepsilon - 1) = 2n &\end{aligned}$$

This results in the following equation

$$\boxed{f^{''}(y) - 2yf^{'}(y) + 2nf(y) = 0} \tag{11.9}$$

There are many ways to solve this equation. One common approach is via a series expansion.

Let's pursue a power series expansion (polynomials). Also note that we have even and odd solutions by symmetry.

$$\begin{aligned} f_1(y) &= \sum_{m=0}^{\infty} a_{2m} y^{2m} \text{ even} \\ f_2(y) &= \sum_{m=0}^{\infty} a_{2m+1} y^{2m+1} \text{ odd} \end{aligned}$$

Start with the even solution

$$\begin{aligned} f_1(y) &= \sum_{m=0}^{\infty} a_{2m} y^{2m} \\ f_1^{'}(y) &= \sum_{m=0}^{\infty} a_{2m} 2m y^{2m-1} \\ f_1^{''}(y) &= \sum_{m=0}^{\infty} a_{2m} 2m(2m-1) y^{2m-2} \end{aligned}$$

Recast the last expression in terms of powers of y^{2m}

$$f_1^{''}(y) = \sum_{m=0}^{\infty} a_{2m+2}(2m+2)(2m+1) y^{2m}$$

This equivalence can be checked explicitly

Now plug the above expressions for the first and second derivatives into our original expression

$$\begin{aligned} f_1^{''}(y) - 2y f_1^{'}(y) + 2n f_1(y) &= 0 \\ \sum_{m=0}^{\infty} a_{2m+2}(2m+2)(2m+1) y^{2m} - \sum_{m=0}^{\infty} 2a_{2m} 2m y^{2m} + 2n \sum_{m=0}^{\infty} a_{2m} y^{2m} &= 0 \end{aligned}$$

Consolidate coefficients of y^{2m} yielding

$$\sum [a_{2m+2}(2m+2)(2m+1) - 4a_{2m} m + 2n a_{2m}] y^{2m} = 0$$

Ok, either we have the trivial solution $y = 0$ or the coefficients in brackets must be zero. We do not want the trival solution so therefore

$$\begin{aligned} [a_{2m+2}(2m+2)(2m+1) - 4a_{2m} m + 2n a_{2m}] &= 0 \\ a_{2m+2}(2m+2)(2m+1) - (4m-2n) a_{2m} &= 0 \\ a_{2m+2}(2m+2)(2m+1) &= (4m-2n) a_{2m} \\ a_{2m+2} &= \frac{2(2m-n) a_{2m}}{(2m+2)(2m+1)} \end{aligned}$$

The even coefficients are therefore

$$a_{2m+2} = \frac{(2m-n)a_{2m}}{(m+1)(2m+1)}$$

Do the same for the odd functions

$$\begin{aligned} f_2(y) &= \sum_{m=0}^{\infty} a_{2m+1} y^{2m+1} \\ f_2^{'}(y) &= \sum_{m=0}^{\infty} a_{2m+1}(2m+1) y^{2m} \\ f_2^{''}(y) &= \sum_{m=0}^{\infty} a_{2m+1}(2m+1)(2m) y^{2m-1} \end{aligned}$$

Recast the last expression in powers of $2m+1$

$$f_2^{''}(y) = \sum_{m=0}^{\infty} a_{2m+3}(2m+3)(2m+2) y^{2m+1}$$

The equivalence can be checked explicitly.

Replace the above expressions for the first and second derivatives into our original expression.

$$\begin{aligned} f_2^{''}(y) - 2yf_2^{'}(y) + 2nf_2(y) &= 0 \\ \sum_{m=0}^{\infty} a_{2m+3}(2m+3)(2m+2) y^{2m+1} - \sum_{m=0}^{\infty} 2a_{2m+1}(2m+1) y^{2m+1} + \sum_{m=0}^{\infty} 2na_{2m+1} y^{2m+1} &= 0 \end{aligned}$$

Collect all coefficients of y^{2m+1}

$$\sum_{m=0}^{\infty} [a_{2m+3}(2m+3)(2m+2) - 2a_{2m+1}(2m+1) + 2na_{2m+1}] y^{2m+1} = 0$$

So at this point we either have the trivial solution $y = 0$ or the coefficient in brackets is zero. Clearly we do not want the trivial solution leaving

$$\begin{aligned} a_{2m+3}(2m+3)(2m+2) - 2a_{2m+1}(2m+1) + 2na_{2m+1} &= 0 \\ a_{2m+3}(2m+3)(2m+2) - (2(2m+1) - 2n)a_{2m+1} &= 0 \\ a_{2m+3}(2m+3)(2m+2) - 2[(2m+1) - n]a_{2m+1} &= 0 \\ a_{2m+3}(2m+3)(2m+2) &= 2[(2m+1) - n]a_{2m+1} \end{aligned}$$

The odd coefficients are therefore

$$\boxed{a_{2m+3} = \frac{2[(2m+1)-n]a_{2m+1}}{(2m+3)(2m+2)}} \qquad (11.10)$$

Summary

$$\boxed{a_{2m+2} = \frac{(2m-n)a_{2m}}{(m+1)(2m+1)} \text{ even}} \tag{11.11}$$

$$\boxed{a_{2m+3} = \frac{[(2m+1)-n]a_{2m+1}}{(m+1)(2m+3)} \text{ odd}} \tag{11.12}$$

For the power series to converge the coefficients a_{2m+2} and a_{2m+3} must go to zero. n is an integer in either case.

Since previously we defined

$$\begin{aligned} (\varepsilon - 1) &= 2n \\ \varepsilon &= 2n + 1 \\ \varepsilon &= 2\left(n + \frac{1}{2}\right) \end{aligned}$$

But recall also that we defined $\epsilon = \beta\varepsilon$ yielding

$$\epsilon = 2\beta\left(n + \frac{1}{2}\right)$$

and $\beta = \dfrac{\hbar\omega}{2}$ giving

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

The desired energies are

$$\boxed{\epsilon = \hbar\omega\left(n + \tfrac{1}{2}\right)} \tag{11.13}$$

where $n = 0, 1, 2, 3 \ldots$. These are the energies of the harmonic oscillator.

Now we need to find the wavefunctions.

$$\begin{aligned} f_1(y) &= \sum_{m=0}^{\infty} a_{2m} y^{2m} \\ f_2(y) &= \sum_{m=0}^{\infty} a_{2m+1} y^{2m+1} \end{aligned}$$

These even and odd solutions turn out to be Hermite polynomials. In general, the wavefunction looks like

$$\Psi(y) = f(y)e^{-\frac{y^2}{2}}$$

Putting it all together we have

$$\boxed{\Psi_n(y) = AH_n e^{-\frac{y^2}{2}}} \tag{11.14}$$

where A is a normalization constant. These are the wavefunctions of the harmonic oscillator. If we express it in real units.

$$\boxed{\Psi_n(x) = \left(\frac{m\omega}{\hbar\pi}\right)^{\frac{1}{4}} e^{-\frac{n}{2}} (n!)^{-\frac{1}{2}} e^{-\frac{m\omega x^2}{2\hbar}} H_n\left(\sqrt{\frac{m\omega}{\hbar}}x\right)} \tag{11.15}$$

where $n = 1, 2, 3\ldots$

Chapter 12

Harmonic Oscillator: raising and lowering operators

This is the ladder or raising and lowering operator treatment.

The Hamiltonian is

$$H = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2$$

where $V(r) = \frac{1}{2}m\omega^2 x^2$ and where $\omega = \sqrt{\frac{k}{m}}$, k is the force constant and m is the mass.

$$\boxed{H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x^2} \tag{12.1}$$

Now rescale both the energy and length over to "intelligent" units.

$$\begin{aligned} x &\rightarrow \alpha x \\ \epsilon &\rightarrow \beta\varepsilon \end{aligned}$$

Here α has units of distance and β has units of energy.

Replace these new variables into

$$H\Psi = \epsilon\Psi$$

yielding

$$\begin{aligned}
\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+\frac{1}{2}m\omega^2x^2\right)\Psi &= \epsilon\Psi \\
\left(-\frac{\hbar^2}{2m}\left(\frac{1}{\alpha^2}\right)\frac{d^2}{dx^2}+\frac{1}{2}m\omega^2\alpha^2x^2\right)\Psi &= \beta\varepsilon\Psi \\
\frac{1}{\beta}\left[-\frac{\hbar^2}{2m}\left(\frac{1}{\alpha^2}\right)\frac{d^2}{dx^2}+\frac{1}{2}m\omega^2\alpha^2x^2\right]\Psi &= \varepsilon\Psi \\
\frac{\hbar^2}{m\alpha^2\beta}\left[-\frac{1}{2}\frac{d^2}{dx^2}+\frac{1}{2}\frac{m^2\omega^2\alpha^4x^2}{\hbar^2}\right]\Psi &= \varepsilon\Psi \\
\frac{\hbar^2}{m\alpha^2\beta}\left[-\frac{1}{2}\frac{d^2}{dx^2}+\frac{x^2}{2}\left(\frac{m^2\omega^2\alpha^4}{\hbar^2}\right)\right]\Psi &= \varepsilon\Psi
\end{aligned}$$

Now define

$$\boxed{\frac{\hbar^2}{m\alpha^2\beta}=1} \tag{12.2}$$

$$\boxed{\frac{m^2\omega^2\alpha^4}{\hbar^2}=1} \tag{12.3}$$

From these two equations we obtain

$$\boxed{\beta=\hbar\omega} \tag{12.4}$$

$$\boxed{\alpha=\sqrt{\frac{\hbar}{m\omega}}} \tag{12.5}$$

Now back to our original problem. Using $\frac{\hbar^2}{m\alpha^2\beta}=1$ and $\frac{m^2\omega^2\alpha^4}{\hbar^2}=1$ our expression becomes

$$\left[-\frac{1}{2}\frac{d^2}{dx^2}+\frac{x^2}{2}\right]\Psi=\varepsilon\Psi$$

or $H\Psi=\varepsilon\Psi$ where

$$\boxed{H=-\frac{1}{2}\frac{d^2}{dx^2}+\frac{x^2}{2}} \tag{12.6}$$

This is our new Hamiltonian.

Now we introduce our raising and lowering operators (also called ladder operators).

$$\boxed{a=\frac{1}{\sqrt{2}}(x+ip)} \tag{12.7}$$

$$\boxed{a^\dagger=\frac{1}{\sqrt{2}}(x-ip)} \tag{12.8}$$

where a is the lowering or annihilation operator and $a^\dagger$ is the raising or creation operator.

At this point we will need some additional pieces of information. First in our intelligent units $\hbar = 1$ so the commutator between position and momentum is

$$[x,p] = i\hbar \rightarrow [x,p] = i$$

Let's check to refresh our memory on commutators

Brief aside

$$[x,p]|\Psi >= (xp - px)|\Psi >$$

where Ψ is a test function. Recall that when working with commutators its easiest to use a dummy test function so you don't get confused.

$$\begin{aligned}
&= -xi\hbar\frac{d\Psi}{dx} + i\hbar\frac{d}{dx}(x\Psi) \\
&= i\hbar\left[-x\frac{d\Psi}{dx} + x\frac{d\Psi}{dx} + \Psi\right] \\
&= i\hbar\Psi \\
&= i\hbar|\Psi >
\end{aligned}$$

So in our case $\hbar = 1$ and $[x,p] = i$.

We will also need $(a^\dagger a)$

$$\begin{aligned}
a^\dagger a &= \frac{1}{2}(x - ip)(x + ip) \\
&= \frac{1}{2}\left[x^2 + ixp - ipx + p^2\right] \\
&= \frac{1}{2}\left[x^2 + p^2 + i[x,p]\right] \\
&= \frac{1}{2}\left[x^2 + p^2 + i(i)\right] \\
&= \frac{1}{2}\left[x^2 + p^2 - 1\right] \\
&= \left(\frac{p^2}{2} + \frac{x^2}{2}\right) - \frac{1}{2} \\
&= H - \frac{1}{2}
\end{aligned}$$

Therefore

$$\boxed{a^\dagger a = H - \tfrac{1}{2}} \tag{12.9}$$

Alternatively

$$\boxed{H = a^\dagger a + \tfrac{1}{2}} \tag{12.10}$$

Let's now define the "number" operator N

$$\boxed{N = a^\dagger a} \tag{12.11}$$

so that

$$\boxed{H = N + \tfrac{1}{2}} \tag{12.12}$$

We will need some more commutators

First, $[a, a^\dagger]$

$$\begin{aligned}
[a, a^\dagger] &= \frac{1}{2}[x + ip, x - ip] \\
&= \frac{1}{2}[(x + ip)(x - ip) - (x - ip)(x + ip)] \\
&= \frac{1}{2}[(x^2 - ixp + ipx + p^2) - (x^2 + ixp - ipx + p^2)] \\
&= \frac{1}{2}[(-ixp + ipx) - (ixp - ipx)] \\
&= \frac{i}{2}[(px - xp) - (xp - px)] \\
&= \frac{i}{2}[[p, x] - [x, p]] \\
&= \frac{i}{2}[-i - i] \\
&= \frac{i}{2}(-2i) \\
&= 1
\end{aligned}$$

Therefore

$$\boxed{[a, a^\dagger] = 1} \tag{12.13}$$

Second, $[a^\dagger, a]$

Likewise, it can be shown that $[a^\dagger, a] = -1$

$$\begin{aligned}
&= \frac{1}{2}[(x-ip),(x+ip)] \\
&= \frac{1}{2}[(x-ip)(x+ip)-(x+ip)(x-ip)] \\
&= \frac{1}{2}[(x^2+ixp-ipx+p^2)-(x^2-ixp+ipx+p^2)] \\
&= \frac{1}{2}[(ixp-ipx)-(-ixp+ipx)] \\
&= \frac{i}{2}[(xp-px)-(px-xp)] \\
&= \frac{i}{2}[[x,p]-[p,x]] \\
&= \frac{i}{2}[i-(-i)] \\
&= \frac{i}{2}(2i) \\
&= -1
\end{aligned}$$

Therefore

$$\boxed{[a^\dagger a] = -1} \tag{12.14}$$

Third, $[N, a]$

$$[N,a] = [a^\dagger a, a]$$

Here we invoke some important commutator relations

$$\boxed{[a,bc] = [a,b]c + b[a,c]} \tag{12.15}$$

$$\boxed{[ab,c] = a[b,c] + [a,c]b} \tag{12.16}$$

$$\begin{aligned}
&= a^\dagger[a,a] + [a^\dagger,a]a \\
&= [a^\dagger,a]a
\end{aligned}$$

where we just showed that $[a^\dagger, a] = -1$

$$= -a$$

Therefore

$$\boxed{[N,a] = -a} \tag{12.17}$$

Fourth, $[N, a^\dagger]$

Likewise it can be shown that $[N, a^\dagger] = a^\dagger$

$$\begin{aligned} &= [a^\dagger a, a^\dagger] \\ &= a^\dagger[a, a^\dagger] + [a^\dagger, a^\dagger]a \\ &= a^\dagger[a, a^\dagger] \\ &= a^\dagger \end{aligned}$$

Therefore

$$\boxed{[N, a^\dagger] = a^\dagger} \tag{12.18}$$

Eigenvalues of N

Now let's go find the eigenvalues of N. Assume that there exists an eigenstate of N denoted by $|n>$ with an eigenvalue λ_n

$$N|n >= \lambda_n|n >$$

Claim that

$$\begin{aligned} N(a|n >) &= (\lambda_n - 1)(a|n >) \\ \text{where we call } |n^{'} >= a|n > & \\ N|n^{'} > &= (\lambda_n - 1)|n^{'} > \end{aligned}$$

That is $|n^{'} >$ is also an eigenstate of N but with an eigenvalue decreased by one energy unit. In other words, "a" acing on $|n >$ results in an eigenstate whose energy is lowered by one energy unit ("a" is a lowering operator)

Proof:

$$\begin{aligned} N(a|n >) &= Na|n > \\ &= (aN + [N, a])\,|n > \\ &= (aN - a)|n > \\ \text{where } [N, a] = -a & \\ &= aN|n > -a|n > \\ &= a\lambda_n|n > -a|n > \\ &= a(\lambda_n - 1)|n > \\ &= (\lambda_n - 1)a|n > \end{aligned}$$

therefore

$$\boxed{N(a|n>) = (\lambda_n - 1)(a|n>)} \tag{12.19}$$

By the same token, $a^\dagger$ is a raising operator.

$$\begin{aligned} N(a^\dagger|n>) = Na^\dagger|n> & \\ &= [a^\dagger N + [N, a^\dagger]]|n> \\ &= (a^\dagger N + a^\dagger)|n> \\ \text{where recall that } [N, a^\dagger] = a^\dagger & \\ &= a^\dagger N|n> + a^\dagger|n> \\ &= \lambda_n a^\dagger|n> + a^\dagger|n> \\ &= (\lambda_n + 1)(a^\dagger|n>) \end{aligned}$$

resulting in

$$\boxed{N(a^\dagger|n>) = (\lambda_n + 1)(a^\dagger|n>)} \tag{12.20}$$

We can apply a and $a^\dagger$ as many times as we like

$$\boxed{N(a^m|n>) = (\lambda_n - m)(a^m|n>)} \tag{12.21}$$

$$\boxed{N(a^{m^\dagger}|n>) = (\lambda_n + m)(a^{m^\dagger}|n>)} \tag{12.22}$$

But there is a lower bound since $V(x) \geq 0$ and $N = H - \frac{1}{2}$. So N is bounded below. We will use this to our advantage especially when finding wavefunctions.

$$\begin{aligned} N|0> &= 0|0>= 0 \\ &\text{or} \\ a|0> &= 0 \end{aligned}$$

terminates the ladder.

Since

$$\begin{aligned} N|n> &= \lambda_n|n> \\ N|n> &= n|n> \end{aligned}$$

In this respect, N is called the number operator because its eigenvalue gives the integer number of quanta of vibrations in the harmonic oscillator problem.

Also since $H = N + \frac{1}{2}$ and $H\Psi = \varepsilon\Psi$

$$\begin{aligned} H|n> &= (N + \frac{1}{2})|n> \\ &= n|n> + \frac{1}{2}|n> \\ &= (n + \frac{1}{2})|n> \end{aligned}$$

leaving

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

in our intelligent units.

Recall $\epsilon = \beta\varepsilon$ where $\beta = \hbar\omega$

$$\boxed{\epsilon = \hbar\omega(n + \tfrac{1}{2})} \tag{12.23}$$

and $n = 0, 1, 2, 3 \ldots$

Now that we have the energies we need the wavefunctions. Use

- $a|0> = 0$
- $a = \frac{1}{\sqrt{2}}(x + ip) = \frac{1}{\sqrt{2}}\left(\frac{d}{dx} + x\right)$

where recall that $p = -i\frac{d}{dx}$ in our intelligent units.

$$\begin{aligned} a|0> &= 0 \\ \frac{1}{\sqrt{2}}\left(\frac{d}{dx} + x\right)\Psi &= 0 \\ \frac{1}{\sqrt{2}}\left(\frac{d\Psi}{dx} + x\Psi\right) &= 0 \\ \frac{d\Psi}{dx} &= -x\Psi \\ \frac{d\Psi}{\Psi} &= -x \\ ln\Psi &= -\frac{x^2}{2} \end{aligned}$$

leaving

$$\Psi_0 = Ce^{-\frac{x^2}{2}}$$

where C is some constant of integration.

$$\boxed{|0>= Ce^{-\frac{x^2}{2}}} \tag{12.24}$$

Now we must normalize the ground state wavefunction $\Psi^*\Psi = 1$ or $< 0|0 >= 1$

$$\begin{aligned} < 0|0 > &= C^2 \int d^{-x^2} dx = 1 \\ &= C^2\sqrt{\pi} = 1 \end{aligned}$$

therefore

$$\begin{aligned} C^2 &= \frac{1}{\sqrt{\pi}} \\ C &= \left(\frac{1}{\pi}\right)^{\frac{1}{4}} \end{aligned}$$

$$\boxed{|0 >= \left(\tfrac{1}{\pi}\right)^{\frac{1}{4}} e^{-\frac{x^2}{2}}} \tag{12.25}$$

in dimensionless units. With units back in we have

$$\boxed{|0 >= \left(\tfrac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}} e^{-\frac{x^2 m\omega}{2\hbar}}} \tag{12.26}$$

where $a^2 = \left(\frac{\hbar}{m\omega}\right)$

Now to get higher eigenstate wavefunctions we will apply $a^\dagger|n >= C_n|n+1 >$ where C_n is a constant and can be found by as follows.

Find C_n

$$\begin{aligned} a^\dagger|n > &= C_n|n+1 > \\ |a^\dagger n > &= C_n|n+1 > \\ < a^\dagger n|a^\dagger n > &= C_n^2 < n+1|n+1 > \\ C_n^2 &= < n|aa^\dagger|n > \\ \text{where recall that } aa^\dagger = (a^\dagger a + [a, a^\dagger]) & \\ C_n^2 &= < n|a^\dagger a + [a, a^\dagger]|n > \\ \text{and that } [a, a^\dagger] = 1 \text{ also } N = a^\dagger a & \\ C_n^2 &= < n|N+1|n > \\ &= < n|N|n > + < n|n > \\ &= n+1 \end{aligned}$$

so that

$$\boxed{C_n = \sqrt{n+1}} \tag{12.27}$$

therefore

$$\boxed{a^\dagger|n> = \sqrt{n+1}|n+1>} \tag{12.28}$$

Find C_{n-1}

Since we're here, let's do the converse and through normalization find C_{n-1}

$$\begin{aligned}
a|n> &= C_{n-1}|n-1> \\
|an> &= C_{n-1}|n-1> \\
<an|an> &= (C_{n-1})^2 <n-1|n-1> \\
C_{n-1}^2 &= <n|a^\dagger a|n> \\
\text{where recall that } a^\dagger a = N & \\
C_{n-1}^2 &= <n|N|n> \\
C_{n-1}^2 &= n
\end{aligned}$$

leaving

$$\boxed{C_{n-1} = \sqrt{n}} \tag{12.29}$$

$$\boxed{a|n> = \sqrt{n}|n-1>} \tag{12.30}$$

Now back to our original problem which was to find the wavefunctions. We will employ the relation $a^\dagger|n> = \sqrt{n+1}|n+1>$. Rearrange it to look like

$$|n+1> = \frac{1}{\sqrt{n+1}}a^\dagger|n>$$

So you can see that if you have one wavefunction, you can find the one above it and continue in this fashion to get all other wavefunctions. So starting withn $|0>$ we get $|1>$ as shown below.

$$\begin{aligned}
|1> &= a^\dagger|0> \\
|2> &= \frac{1}{\sqrt{2}}a^\dagger|1> = \frac{1}{\sqrt{2}}(a^\dagger)^2|0> \\
\text{etc.}\ldots & \\
|n> &= \frac{1}{\sqrt{n!}}(a^\dagger)^n|0>
\end{aligned}$$

where $a^\dagger = \frac{1}{\sqrt{2}}(x - ip) = \frac{1}{\sqrt{2}}\left(x - \frac{d}{dx}\right)$

$$\boxed{\Psi_n(x) = \frac{1}{\sqrt{2^n n!}}\left(x - \frac{d}{dx}\right)^n \left[(\tfrac{1}{\pi})^{\frac{1}{4}} e^{-\frac{x^2}{2}}\right]} \tag{12.31}$$

It turns out that this is another way of writing the Hermite polynomials.

Summary

So to summarize, here is a recap of useful identities. In units where $m = \omega = \hbar = 1$ and with the energy in units of $\hbar\omega$ and the length in units of $\sqrt{\frac{\hbar}{m\omega}}$

$$\boxed{H = \frac{p^2}{2} + \frac{x^2}{2}} \tag{12.32}$$

$$\boxed{a = \frac{1}{\sqrt{2}}(x + ip)} \tag{12.33}$$

$$\boxed{a^\dagger = \frac{1}{\sqrt{2}}(x - ip)} \tag{12.34}$$

$$\boxed{x = \frac{1}{\sqrt{2}}(a^\dagger + a)} \tag{12.35}$$

$$\boxed{p = \frac{i}{\sqrt{2}}(a^\dagger - a)} \tag{12.36}$$

$$\boxed{[x, p] = i} \tag{12.37}$$

$$\boxed{[a, a^\dagger] = 1} \tag{12.38}$$

$$\boxed{N = a^\dagger a} \tag{12.39}$$

$$\boxed{H = N + \frac{1}{2}} \tag{12.40}$$

$$\boxed{H|n >= (n + \frac{1}{2})|n >} \tag{12.41}$$

$$\boxed{a^\dagger|n >= \sqrt{n+1}|n+1 >} \tag{12.42}$$

$$\boxed{a|n >= \sqrt{n}|n-1 >} \tag{12.43}$$

Chapter 13

Rigid Rotor

The classical angular momentum is $L = I\omega$ where I is the moment of inertia, ω is the angular velocity, $I = \mu r^2$ where μ is the reduced mass $\left(\mu = \frac{m_1 m_2}{(m_1+m_2)}\right)$ and r is the separation between the particle of reduced mass and the origin.

Quantum mechanically since there are no external forces in this problem (no potential energy term) the Hamiltonian operator is just the kinetic energy operator.

$$H = -\frac{\hbar^2 \nabla^2}{2\mu}$$

and

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

This is the Laplacian in spherical coordinates.

Since r is a constant there is no need for $\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)$.

The Laplacian therefore simplifies to

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

Then the Hamiltonian becomes

$$\begin{aligned} H &= -\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2 sin\theta}\frac{\partial}{\partial\theta}\left(sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{r^2 sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right] \\ &= -\frac{\hbar^2}{2\mu r^2}\left[\frac{1}{sin\theta}\frac{\partial}{\partial\theta}\left(sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{sin^2\theta}\frac{\partial^\theta}{\partial\phi^2}\right] \end{aligned}$$

where recall that $I = \mu r^2$

$$= -\frac{\hbar^2}{2I}\left[\frac{1}{sin\theta}\frac{\partial}{\partial\theta}\left(sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$$

Note that the expression in brackets is really the quantum mechanical angular momentum operator.

$$\boxed{L^2 = -\hbar^2\left[\frac{1}{sin\theta}\frac{\partial}{\partial\theta}\left(sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]} \tag{13.1}$$

Now we have

$$\boxed{H = -\frac{L^2}{2I}} \tag{13.2}$$

for the rigid rotor.

The time independent Schrodinger equation we derived earlier is just an eigenvector eigenvalue problem $H\Psi = \epsilon\Psi$ where the wavefunction $\Psi(\theta,\phi)$ is a function of both θ and ϕ. We have

$$-\frac{\hbar^2}{2I}\left[\frac{1}{sin\theta}\frac{\partial}{\partial\theta}\left(sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\Psi(\theta,\phi) = \epsilon\Psi(\theta,\phi)$$

Multiply both sides by $sin^2\theta$

$$-\frac{\hbar^2}{2I}[sin\theta\frac{\partial}{\partial\theta}\left(sin\theta\frac{\partial}{\partial\theta}\right)+\frac{\partial^2}{\partial\theta^2}]\Psi(\theta,\phi) = \epsilon sin^2\theta\Psi(\theta,\phi)$$

Multiply both sides by $-\frac{2I}{\hbar^2}$ to clear the front of the left hand side

$$\left[sin\theta\frac{\partial}{\partial\theta}\left(sin\theta\frac{\partial}{\partial\theta}\right)+\frac{\partial^2}{\partial\phi^2}\right]\Psi(\theta,\phi) = -\frac{2I\epsilon}{\hbar^2}sin^2\theta\Phi(\theta,\phi)$$

Let $\beta = \frac{2I\epsilon}{\hbar^2}$

$$\left[sin\theta\frac{\partial}{\partial\theta}\left(sin\theta\frac{\partial}{\partial\theta}\right)+\frac{\partial^2}{\partial\phi^2}\right]\Psi(\theta,\phi)+\beta sin^2\theta\Psi(\theta,\phi) = 0$$

Apply the method of separation of variables to evaluate the last expression. Choose $\Psi(\theta,\phi) = \Theta\Phi = TF$ (for shorthand).

Replace this into our previous expression

$$\begin{aligned}\left[sin\theta\frac{\partial}{\partial\theta}\left(sin\theta\frac{\partial}{\partial\theta}\right)+\frac{\partial^2}{\partial\phi^2}\right]TH+\beta sin^2\theta TF &= 0\\ sin\theta\frac{\partial}{\partial\theta}\left(sin\theta\frac{\partial(TF)}{\partial\theta}\right)+\frac{\partial^2(TF)}{\partial\phi^2}+\beta sin^2\theta TF &= 0\end{aligned}$$

As an aside

$$\begin{aligned}\frac{\partial^2(TF)}{\partial\phi^2} &= \frac{\partial}{\partial\phi}\left(\frac{\partial(TF)}{\partial\phi}\right)\\ &= \frac{\partial}{\partial\phi}\left[T\frac{\partial F}{\partial\phi}+F\frac{\partial T}{\partial\phi}\right]\end{aligned}$$

note that T doesn't have a ϕ dependence

$$\begin{aligned}&= \frac{\partial}{\partial\phi}\left[T\frac{\partial E}{\partial\phi}\right]\\ &= T\frac{\partial^2 F}{\partial\phi^2}+\frac{\partial F}{\partial\phi}\frac{\partial T}{\partial\phi}\\ &= T\frac{\partial^2 F}{\partial\phi^2}\end{aligned}$$

From this we can go back to our original expression and get

$$\begin{aligned}sin\theta\frac{\partial}{\partial\theta}\left[sin\theta\left(T\frac{\partial F}{\partial\theta}+F\frac{\partial T}{\partial\theta}\right)\right]+T\frac{\partial^2 F}{\partial\phi^2}+\beta sin^2\theta TF &= 0\\ sin\theta\frac{\partial}{\partial\theta}\left[sin\theta F\frac{\partial T}{\partial\theta}\right]+T\frac{\partial^2 F}{\partial\phi^2}+\beta sin^2\theta TF &= 0\\ sin\theta F\frac{\partial}{\partial\theta}\left(sin\theta\frac{\partial T}{\partial\theta}\right)+T\frac{\partial^2 F}{\partial\phi^2}+\beta sin^2\theta TF &= 0\\ \text{divide by } TF \text{ to simplify}&\\ \frac{sin\theta}{T}\frac{\partial}{\partial\theta}\left(sin\theta\frac{\partial T}{\partial\theta}\right)+\frac{1}{F}\frac{\partial^2 F}{\partial\phi^2}+\beta sin^2\theta &= 0\end{aligned}$$

Notice that you have one part that depends solely on θ and another that depends solely on ϕ

$$\frac{sin\theta}{T}\frac{\partial}{\partial\theta}\left(sin\theta\frac{\partial T}{\partial\theta}\right)+\beta sin^2\theta=-\frac{1}{F}\frac{\partial^2 F}{\partial\phi^2}$$

Since they are equivalent they both must equal a constant. Call the constant m^2 for convenience.

$$\boxed{\frac{sin\theta}{T}\frac{\partial}{\partial\theta}\left(sin\theta\frac{\partial T}{\partial\theta}\right)+\beta sin^2\theta=m^2} \tag{13.3}$$

$$\boxed{-\frac{1}{F}\frac{\partial^2 F}{\partial\phi^2}=m^2} \tag{13.4}$$

Solve the second equation first.

$$\frac{d^2F}{d\phi^2}+m^2F=0$$

A general solution of this is of the form

$$F=ae^{im\phi}$$

By continuity

$$\begin{aligned} F(\phi) &= F(\phi+2\pi) \\ F(\phi+2\pi) &= ae^{im(\phi+2\pi)}=F(\phi) \\ ae^{im\phi}e^{im2\pi} &= ae^{im\phi} \end{aligned}$$

therefore

$$\begin{aligned} e^{im2\pi} &= 1 \\ e^{im2\pi} &= cos2\pi m+isin2\pi m=1 \end{aligned}$$

To be true the restrictions on m are $m=0,\pm1,\pm2,\pm3\ldots$

Now go back and look at the second equation.

$$\frac{sin\theta}{T}\frac{\partial}{\partial\theta}\left(sin\theta\frac{\partial T}{\partial\theta}\right)+\beta sin^2\theta=m^2$$

Let $x=cos\theta$, $x^2=cos^2\theta$. Now relabel T as P which is a function of x. From this we have $1-x^2=sin^2\theta$ and also $\sqrt{1-x^2}=sin\theta$

$$\begin{aligned} \frac{\sqrt{1-x^2}}{P}\frac{\partial}{\partial\theta}[\sqrt{1-x^2}\frac{dP}{d\theta}]+\beta(1-x^2) &= m^2 \\ \sqrt{1-x^2}\frac{d}{d\theta}\left[\sqrt{1-x^2}\frac{dP}{d\theta}\right]+[\beta(1-x^2)-m^2]P &= 0 \end{aligned}$$

Now we have $\frac{dx}{d\theta} = -sin\theta$ and then $d\theta = -\frac{dx}{sin\theta} = \frac{-dx}{\sqrt{1-x^2}}$ then finally $\frac{d}{d\theta} = -sin\theta\frac{d}{dx}$

$$\begin{aligned}
-(\sqrt{1-x^2})(\sqrt{1-x^2})\frac{d}{dx}\left[\sqrt{1-x^2}\frac{dP}{dx}(-\sqrt{1-x^2})\right] + [\beta(1-x^2) - m^2]P &= 0 \\
(1-x^2)\frac{d}{dx}\left[(1-x^2)\frac{dP}{dx}\right] + [\beta(1-x^2) - m^2]P &= 0 \\
(1-x^2)\left[(1-x^2)\frac{d^2P}{dx^2} + \frac{dP}{dx}(-2x)\right] + [\beta(1-x^2) - m^2]P &= 0 \\
(1-x^2)\frac{d^2P}{dx^2} - 2x(1-x^2)\frac{dP}{dx} + [\beta(1-x^2) - m^2]P &= 0 \\
\text{divide out } (1-x^2)
\end{aligned}$$

giving

$$\boxed{(1-x^2)\frac{d^2P}{dx^2} - 2x\frac{dP}{dx} + \left[\beta - \frac{m^2}{(1-x^2)}\right]P = 0} \qquad (13.5)$$

This is called Legendre's equation or actually the associated Legendre differential equation. In Abramowitz and Stegun the definition is

$$\boxed{(1-x^2)\frac{d^2y}{dx^2} - 2x\frac{dy}{dx} + \left[l(l+1) - \frac{m^2}{(1-x^2)}\right]y = 0} \qquad (13.6)$$

if l is an integer then the solutions $P_l^m(x)$ are called the associated Legendre polynomials. If l is not an integer then the solutions are called the Legendre polynomials of the 1st kind. We will deal with the former.

Now clearly we want $\beta = l(l+1)$ but let's show that explicitly.

$$(1-x^2)\frac{d^2P}{dx^2} - 2x\frac{dP}{dx} + \left[\beta - \frac{m^2}{(1-x^2)}\right]P = 0$$

Consider the case $m = 0$ yielding

$$(1-x^2)\frac{d^2P}{dx^2} - 2x\frac{dP}{dx} + \beta P = 0$$

Consider that P can be represented as a polynomial in powers of k (or λ, or whatever you want to call it)

$$P = \sum a_k x^k$$

where $k = 0, 1, 2, 3 \ldots (k-1), k$. Now plug this power series solution into the above equation.

$$\begin{aligned}
\frac{dP}{dx} &= \sum a_k k x^{k-1} \\
2x\frac{dP}{dx} &= \sum 2a_k k x^k
\end{aligned}$$

Now get the second derivative

$$\begin{aligned}
\frac{d^2P}{dx^2} &= \sum a_k k(k-1)x^{k-2} \text{ in powers of } x^{k-2} \\
&= \sum a_{k+2}(k+1)(k+2)x^k \text{ in powers of } x^k
\end{aligned}$$

Replacing this into our original equation we have

$$\begin{aligned}
(1-x^2)\frac{d^2P}{dx^2} - 2x\frac{dP}{dx} + \beta P &= 0 \\
\frac{d^2P}{dx^2} - x^2\frac{d^2P}{dx^2} - 2x\frac{dP}{dx} + \beta P &= 0
\end{aligned}$$

Keep things in powers of x^k

$$\sum a_{k+2}(k+1)(k+2)x^k - \sum a_k k(k-1)x^k - \sum 2a_k k x^k + \beta \sum a_k x^k = 0$$

Note that everything is expressed in terms of x^k. Collect its coefficients.

$$\sum [a_{k+2}(k+1)(k+2) - a_k k(k-1) - 2a_k k + \beta a_k] x^k = 0$$

So either $x = 0$ (the trivial solution) or the coefficients in brackets must equal zero. Like always we do not want the trivial solution. Therefore

$$\begin{aligned}
a_{k+2}(k+1)(k+2) - a_k k(k-1) - 2a_k k + \beta a_k &= 0 \\
a_{k+2}[(k+1)(k+2)] - a_k[k(k-1) + 2k - \beta] &= 0 \\
a_{k+2}[(k+1)(k+2)] - a_k[k^2 - k + 2k - \beta] &= 0 \\
a_{k+2}[(k+1)(k+2)] - a_k[k(k+1) - \beta] &= 0 \\
a_{k+2}[(k+1)(k+2)] &= a_k[k(k+1) - \beta]
\end{aligned}$$

This yields

$$\boxed{a_{k+2} = \frac{a_k[k(k+1)-\beta]}{(k+1)(k+2)}} \tag{13.7}$$

alternatively

$$\boxed{\left(\frac{a_{k+2}}{a_k}\right) = \frac{k}{k+2} - \frac{\beta}{(k+1)(k+2)}} \tag{13.8}$$

As $k \to \infty$ we have $\left(\frac{a_{k+2}}{a_k}\right) \to 1$. To have this power series converge $a_{k+2} \to 0$. So with $a_{k+2} = 0$ we have

$$\begin{aligned} \frac{k}{k+2} &= \frac{\beta}{(k+1)(k+2)} \\ k &= \frac{\beta}{(k+1)} \end{aligned}$$

we therefore have

$$\boxed{\beta = k(k+1)} \tag{13.9}$$

replace k with l

$$\boxed{\beta = l(l+1)} \tag{13.10}$$

where $l = 0, 1, 2, 3 \ldots$.

Ok, now that we have this result let's go back to our main equation.

$$(1-x^2)\frac{d^2P}{dx^2} - 2x\frac{dP}{dx} + \left[l(l+1) - \frac{m^2}{1-x^2}\right]P = 0$$

whose solutions are called associated Legendre polynomials. Recall also that $\beta = \frac{2I\epsilon}{\hbar^2}$ resulting in

$$l(l+1) = \frac{2I\epsilon}{\hbar^2}$$

Solving for ϵ we have

$$\boxed{\epsilon = \frac{\hbar^2 l(l+1)}{2I}} \tag{13.11}$$

These are the energies of the rigid rotor problem where again $l = 0, 1, 2, 3 \ldots$.

Now note that we want our associated Legendre polynomials as a function of θ instead of x. Recall that $x = cos\theta$. Skipping a lot of work we have

$$\Psi(\theta, \phi) \equiv Y_l^m(\theta, \phi) = \left[\frac{2l+1}{4\pi}\frac{(l-|m|)!}{(l+|m|)!}\right]^{\frac{1}{2}} P_l^m(cos\theta)e^{im\phi}$$

Here $\Psi(\theta, \phi) \equiv Y_l^m(\theta, \phi)$ are called spherical harmonics and have the functional form

$$\boxed{Y_l^m(\theta, \phi) = \left[\frac{2l+1}{4\pi}\frac{(l-|m|)!}{(l+|m|)!}\right]^{\frac{1}{2}} P_l^m(cos\theta)e^{im\phi}} \tag{13.12}$$

These are our desired wavefunctions.

$$\boxed{\epsilon = \frac{\hbar^2 l(l+1)}{2I}} \tag{13.13}$$

These are our desired energies.

Chapter 14

Selection Rules

Harmonic Oscillator

Derive the selction rules for transitions between vibrational levels of a molecule modeled as a harmonic oscillator. Neglect rotational transitions. These rules govern the absorption of infrared radiation.

Expand μ about the equilibrium nucleus separation.

$$\mu = \mu_0 + \left(\frac{\partial \mu}{\partial q}\bigg|_{x_0} \right) + \ldots$$

Ignore higher order terms.

The transition dipole moment is

$$\begin{array}{r} < n^{'} | \mu | n > \\ < n^{'} | \mu_0 + \frac{\partial \mu}{\partial q} q | n > \\ < n^{'} | \mu_0 | n > + \frac{\partial \mu}{\partial q}\bigg|_{q_0} < n^{'} | q | n > \\ \mu_0 < n^{'} | n > + \frac{\partial \mu}{\partial q}\bigg|_{q_0} < n^{'} | q | n > \end{array}$$

The first term is zero unless $n = n^{'}$ and to evaluate the second term recall that $q \propto (a + a^{\dagger})$ (raising and lowering operators)

$$\begin{aligned} &= const < n^{\dagger} | a + a^{\dagger} | n > \\ &= const[< n^{\dagger} | a | n > + < n^{'} | a^{\dagger} | n >] \end{aligned}$$

where

- $a|n>=\sqrt{n}|n-1>$
- $a^{\dagger}|n>=\sqrt{n+1}|n+1>$

this leaves

$$=const[const<n^{'}|n-1>+const<n^{'}|n+1>]$$

So to be nonzero

$$\boxed{\Delta n=\pm 1} \tag{14.1}$$

This is the desired selection rule for the harmonic oscillator.

Rigid Rotor

Derive the selection rules for transitions between rotational levels of a heteronuclear diatomic molecule. These rules govern the absorption of far infrared (microwave) radiation.

Treat the molecule as a rigid rotor.

$$\Psi(\theta,\phi)=Y_l^m(\theta,\phi)=|l,m>$$

By symmetry the dipole is oriented along the molecule.

$$\mu=\mu_0(cos\phi sin\theta\hat{x}+sin\phi sin\theta\hat{y}+cos\theta\hat{z})$$

Assume $\hat{z}$ polarization for the field to make life easier.

$$\mu=\mu_0 cos\theta\hat{z}$$

The transition dipole moment is

$$<l^{'},m^{'}|\mu|l,m>\propto<l^{'},m^{'}|cos\theta|l,m>$$

Now we make use of a relation

$$\boxed{cos\theta Y_l^m(\theta,\phi)=\sqrt{\frac{(l+m+1)(l-m+1)}{(2l+1)(2l+3)}}Y_{l+1}^m(\theta,\phi)+\sqrt{\frac{(l+m)(l-m)}{(2l+1)(2l-1)}}Y_{l-1}^m(\theta,\phi)} \tag{14.2}$$

Therefore

$$cos\theta|l,m>=a|l+1,m>+b|l-1,m>$$

where

$$\begin{aligned} a &= \sqrt{\frac{(l+m+1)(l-m+1)}{(2l+1)(2l+3)}} \\ b &= \sqrt{\frac{(l+m)(l-m)}{(2l+1)(2l-1)}} \end{aligned}$$

leaving

$$< l^{'}, m^{'} | \; [a|l+1, m> + b|l-1, m>]$$
$$= a < l^{'}, m^{'} | l+1, m> + b < l^{'}, m^{'} | l-1, m>$$

To be nonzero

$$\boxed{\Delta l = \pm 1} \tag{14.3}$$

$$\boxed{\Delta m = 0} \tag{14.4}$$

These are the desired selection rules for the rigid rotor.

Rovibrations

Now consider rotational/vibrational transitions of a molecule. Here we are concerned with mid-infrared absorption from the ground vibrational level to the 1st excited vibrational level with changes in the rotational energy. Derive the selection rules for these transitions.

Assume $\hat{z}$ polarization for simplicity.

$$|\Psi> = |n> |l, m>$$

and where

$$\begin{aligned} \mu &= \mu(q)(cos\phi sin\theta\hat{x} + sin\phi sin\theta\hat{y} + cos\theta\hat{z}) \\ &\text{and} \\ \mu(q) &= \left(\mu_0 + \left.\frac{\partial\mu}{\partial q}\right|_{q_0}\right) + \ldots \end{aligned}$$

we consider only the first two terms in the second expression. This leaves

$$\mu = (\mu_0 + const \cdot q)cos\theta$$

The transition dipole moment is then

$$\begin{aligned} & < l^{'}, m^{'}| < n^{'}|\mu|n > |l, m > \\ = & < n^{'}|\mu(q)|n >< l^{'}, m^{'}|cos\theta|l, m > \\ = & < n^{'}|\mu_0 + const \cdot q|n >< l^{'}, m^{'}|cos\theta|l, m > \\ = & [< n^{'}|\mu_0|n > +const < n^{'}|q|n >] < l^{'}, m^{'}|cos\theta|l, m > \end{aligned}$$

The first term is zero unless $n = n^{'}$ and recall that $q \propto (a + a^{\dagger})$. So from the second term in brackets we get the selection rule

$$\boxed{\Delta n = \pm 1} \tag{14.5}$$

Next we look to the angle dependent term

$$< l^{'}, m^{'}|cos\theta|l, m >$$

where

$$cos\theta|l, m >= const|l + 1, m > +const|l - 1, m >$$

This yields the additional selection rules

$$\boxed{\Delta m = 0} \tag{14.6}$$

$$\boxed{\Delta l = \pm 1} \tag{14.7}$$

Summary

$$\boxed{\Delta n = \pm 1} \tag{14.8}$$

$$\boxed{\Delta m = 0} \tag{14.9}$$

$$\boxed{\Delta l = \pm 1} \tag{14.10}$$

In general $\Delta m = 0, \pm 1$

Chapter 15

Potential Step

The Schrodinger equation to solve is

$$\boxed{-\frac{\hbar^2}{2m}\frac{d^2\Psi}{dx^2} + V\Psi = \epsilon\Psi} \tag{15.1}$$

Our general strategy will be to solve the equation piecewise. We will solve it for region 1 then region 2 and then paste the two parts of the wavefunction together at the interface between regions 1 and 2.

Region 1 (V=0)

$$\begin{aligned} -\frac{\hbar^2}{2m}\frac{d^2\Psi}{dx^2} &= \epsilon\Psi \\ \frac{d^2\Psi}{dx^2} &= -\frac{2m\epsilon}{\hbar^2}\Psi \\ \frac{d^2\Psi}{dx^2} + k^2\Psi &= 0 \end{aligned}$$

where $k^2 = \frac{2m\epsilon}{\hbar^2}$ and $k = \sqrt{\frac{2m\epsilon}{\hbar^2}}$. The solutions of this last equation in general is

$$\boxed{\Psi_1 = Ae^{ikx} + Be^{-ikx}} \tag{15.2}$$

Region 2

Next we solve the Schrodinger equation in region 2. Here there are two possibilities. Either the energy of the particle is larger than V ($\epsilon > V$) or its less than V ($\epsilon < V$).

Case ($\epsilon < V$)

For brevity we just consider one case.

$$\begin{aligned}
-\frac{\hbar^2}{2m}\frac{d^2\Psi}{dx^2} + V\Psi &= \epsilon\Psi \\
-\frac{\hbar^2}{2m}\frac{d^2\Psi}{dx^2} &= (\epsilon - V)\Psi \\
\frac{d^2\Psi}{dx^2} &= -\frac{2m(\epsilon - V)}{\hbar^2}\Psi \\
\frac{d^2\Psi}{dx^2} + \frac{2m(\epsilon - V)}{\hbar^2}\Psi &= 0 \\
\frac{d^2\Psi}{dx^2} - \frac{2m(V - \epsilon)}{\hbar^2}\Psi &= 0 \\
\text{Let } \beta^2 = \frac{2m(V-\epsilon)}{\hbar^2} & \\
\frac{d^2\Psi}{dx^2} - \beta^2\Psi &= 0
\end{aligned}$$

The general solutions to this last equation are

$$\boxed{\Psi_2 = Ce^{\beta x} + De^{-\beta x}} \tag{15.3}$$

Now we need to paste together the two wavefunctions using the so called matching conditions.

$$\boxed{\Psi_1(0) = \Psi_2(0)} \tag{15.4}$$

$$\boxed{\Psi_1^{'}(0) = \Psi_2^{'}(0)} \tag{15.5}$$

This will lead to the following equations.

$$\begin{aligned}
A + B &= C + D \\
ikA - ikB &= \beta C - \beta D \rightarrow A - B = \frac{\beta}{ik}(C - D)
\end{aligned}$$

However we can't have our wavefunction ill behaved. It must be finite valued. So can't blow up in region 2 which defines one of the coefficients. (C=0) Now we will solve for A and B. First do A.

$$\begin{aligned}
A + B &= D \\
A - B &= -\frac{\beta}{ik}D \\
\text{yielding} & \\
2A &= \left(1 - \frac{\beta}{ik}\right) D
\end{aligned}$$

giving

$$\boxed{A = \tfrac{D}{2}\left(1 - \tfrac{\beta}{ik}\right)} \tag{15.6}$$

Next solve for B

$$\begin{aligned}
-A - B &= -D \\
A - B &= -\frac{\beta}{ik}D \\
\text{yielding} & \\
-2B &= -\left(1 + \frac{\beta}{ik}\right)D
\end{aligned}$$

giving

$$\boxed{B = \tfrac{D}{2}\left(1 + \tfrac{\beta}{ik}\right)} \tag{15.7}$$

The fraction of particles reflected is

$$\begin{aligned}
R &= \frac{v_1|B|^2}{v_1|A|^2} = \left|\frac{B}{A}\right|^2 = \frac{B^*B}{A^*A} \\
&= \frac{\frac{D^2}{4}\left(1 + \frac{\beta}{ik}\right)\left(1 - \frac{\beta}{ik}\right)}{\frac{D^2}{4}\left(1 - \frac{\beta}{ik}\right)\left(1 + \frac{\beta}{ik}\right)} \\
&= \frac{\frac{D^2}{4}\left(1 + \frac{\beta^2}{k^2}\right)}{\frac{D^2}{4}\left(1 + \frac{\beta^2}{k^2}\right)} \\
&= 1
\end{aligned}$$

Since $R + T = 1$ we find that $T = 0$. No particles make it through the step even though it can be shown that there is a nonzero probability for finding the particle in the forbidden region.

Chapter 16

Potential Barrier

There are two possibilities here ($\epsilon > V$) and ($\epsilon < V$). We will consider the first case here

Case 1 ($\epsilon > V$)

Assume a source of particles on the left only. What is the behavior of the wavefunction. What is the transmission coefficient $T = \left|\frac{F}{A}\right|^2$. To begin with, we have the following wavefunctions in regions 1, 2, and 3.

$$\begin{aligned} \Psi_1 &= Ae^{ikx} + Be^{-ikx} \\ \Psi_2 &= Ce^{i\phi x} + De^{-i\phi x} \\ \Psi_3 &= Fe^{ikx} + Ge^{-ikx} \end{aligned}$$

Since there is no source of particles on the right, $G = 0$. This leaves

$$\begin{aligned} \Psi_1 &= Ae^{ikx} + Be^{-ikx} \\ \Psi_2 &= Ce^{i\phi x} + De^{-i\phi x} \\ \Psi_3 &= Fe^{ikx} \end{aligned}$$

where k and ϕ are

$$\begin{aligned} k &= \sqrt{\frac{2m\epsilon}{\hbar^2}} \\ \phi &= \sqrt{\frac{2m(\epsilon - V)}{\hbar^2}} \end{aligned}$$

Recall now that we must apply the matching conditions to merge the wavefunctions at the different interfaces.

- $\Psi_1(0) = \Psi_2(0)$
- $\Psi_1^{'}(0) = \Psi_2^{'}(0)$
- $\Psi_2(a) = \Psi_3(a)$
- $\Psi_2^{'}(a) = \Psi_3^{'}(a)$

Using the first two matching conditions we get

$$\begin{aligned} A + B &= C + D \\ ikA - ikB &= i\phi C - i\phi D \end{aligned}$$

leading to

$$\boxed{A + B = C + D} \tag{16.1}$$

$$\boxed{A - B = \tfrac{\phi}{k} C - \tfrac{\phi}{k} D} \tag{16.2}$$

Using the second two matching conditions we get

$$\begin{aligned} Ce^{i\phi a} + De^{-i\phi a} &= Fe^{ika} \\ i\phi Ce^{i\phi a} - i\phi De^{-i\phi a} &= ikFe^{ika} \end{aligned}$$

leading to

$$\boxed{Ce^{i\phi a} + De^{-i\phi a} = Fe^{ika}} \tag{16.3}$$

$$\boxed{Ce^{i\phi a} - De^{-i\phi a} = \tfrac{k}{\phi} Fe^{ika}} \tag{16.4}$$

Now solve for A, B, C, D all in terms of F to make life simple. From the first two equations we get

$$2A = \left(1 + \frac{\phi}{k}\right) C + \left(1 - \frac{\phi}{k}\right) D$$

$$\boxed{A = \tfrac{1}{2}\left(1 + \tfrac{\phi}{k}\right) C + \tfrac{1}{2}\left(1 - \tfrac{\phi}{k}\right) D} \tag{16.5}$$

$$2B = \left(1 - \frac{\phi}{k}\right) C + \left(1 + \frac{\phi}{k}\right) D$$

$$\boxed{B = \tfrac{1}{2}\left(1 - \tfrac{\phi}{k}\right) C + \tfrac{1}{2}\left(1 + \tfrac{\phi}{k}\right) D} \tag{16.6}$$

From the second two equations we get

$$2Ce^{i\phi a} = \left(1+\frac{k}{\phi}\right)Fe^{ika}$$

$$2C = \left(1+\frac{k}{\phi}\right)Fe^{i(k-\phi)a}$$

$$\boxed{C = \tfrac{1}{2}\left(1+\tfrac{k}{\phi}\right)Fe^{i(k-\phi)a}} \tag{16.7}$$

$$2De^{-i\phi a} = \left(1-\frac{k}{\phi}\right)Fe^{ika}$$

$$2D = \left(1-\frac{k}{\phi}\right)Fe^{i(k+\phi)a}$$

$$\boxed{D = \tfrac{1}{2}\left(1-\tfrac{k}{\phi}\right)Fe^{i(k+\phi)a}} \tag{16.8}$$

Now we want the transmission coefficient through the barrier $T = \left|\frac{F}{A}\right|^2$. This means that we need to determine A explicitly in terms of F.

$$\begin{aligned}
A &= \frac{1}{2}\left(1+\frac{\phi}{k}\right)C + \frac{1}{2}\left(1-\frac{\phi}{k}\right)D \\
&= \frac{1}{2}\left(1+\frac{\phi}{k}\right)\left[\frac{1}{2}\left(1+\frac{k}{\phi}\right)Fe^{i(k-\phi)a}\right] + \frac{1}{2}\left(1-\frac{\phi}{k}\right)\left[\frac{1}{2}\left(1-\frac{k}{\phi}\right)Fe^{i(k+\phi)a}\right] \\
&= \frac{1}{4}\left(\frac{k+\phi}{k}\right)\left(\frac{k+\phi}{\phi}\right)Fe^{i(k-\phi)a} + \frac{1}{4}\left(\frac{k-\phi}{k}\right)\left(\frac{\phi-k}{\phi}\right)Fe^{i(k+\phi)a} \\
&= \frac{F}{4k\phi}\left[(k+\phi)^2e^{i(k-\phi)a} - (k-\phi)^2e^{i(k+\phi)a}\right] \\
&\quad \text{call } E_1 = e^{i(k-\phi)a} \text{ and } E_2 = e^{i(k+\phi)a} \\
&= \frac{F}{4k\phi}[(k^2+\phi^2)E_1 + 2k\phi E_1 - ((k^2+\phi^2)E_2 - 2k\phi E_2)] \\
&= \frac{F}{4k\phi}[(k^2+\phi^2)(E_1-E_2) + 2k\phi(E_1+E_2)] \\
&= \frac{F}{4k\phi}[(k^2+\phi^2)(e^{ika}e^{-i\phi a} - e^{ika}e^{i\phi a}) + 2k\phi(e^{ika}e^{-i\phi a} + e^{ika}e^{i\phi a})] \\
&= \frac{Fe^{ika}}{4k\phi}\left[-2i(k^2+\phi^2)\left(\frac{e^{i\phi a}-e^{-i\phi a}}{2i}\right) + 4k\phi(\frac{e^{i\phi a}+e^{-i\phi a}}{2})\right] \\
&= \frac{Fe^{ika}}{4k\phi}[4k\phi cos\phi a - 2i(k^2+\phi^2)sin\phi a]
\end{aligned}$$

yielding

$$\boxed{A = \frac{Fe^{ika}}{4k\phi}[4k\phi cos\phi a - 2i(k^2 + \phi^2)sin\phi a]} \tag{16.9}$$

Though we don't need it right now, we will solve for B

$$\begin{aligned}
B &= \frac{1}{2}\left(1 - \frac{\phi}{k}\right) C + \frac{1}{2}\left(1 + \frac{\phi}{k}\right) D \\
&= \frac{1}{2}\left(1 - \frac{\phi}{k}\right)\left[\frac{1}{2}\left(1 + \frac{k}{\phi}\right) Fe^{i(k-\phi)a}\right] + \frac{1}{2}\left(1 + \frac{\phi}{k}\right)\left[\frac{1}{2}\left(1 - \frac{k}{\phi}\right) Fe^{i(k+\phi)a}\right] \\
&= \frac{F}{4}(\frac{k-\phi}{k})(\frac{k+\phi}{\phi})e^{i(k-\phi)a} + \frac{F}{4}(\frac{k+\phi}{k})(\frac{\phi-k}{\phi})e^{i(k+\phi)a} \\
&= \frac{F}{4k\phi}(k^2 - \phi^2)e^{ika}e^{-i\phi a} - \frac{F}{4k\phi}(k^2 - \phi^2)e^{ika}e^{i\phi a} \\
&= \frac{F}{4k\phi}(k^2 - \phi^2)e^{ika}(e^{-i\phi a} - e^{i\phi a}) \\
&= \frac{2iF}{4k\phi}(\phi^2 - k^2)e^{ika}\left(\frac{e^{i\phi a} - e^{-i\phi a}}{2i}\right) \\
&= \frac{iF}{2k\phi}(\phi^2 - k^2)e^{ika}sin\phi a
\end{aligned}$$

leaving

$$\boxed{B = \frac{iF(\phi^2 - k^2)}{2k\phi}e^{ika}sin\phi a} \tag{16.10}$$

Now we are in a position to evaluate our desired transmission and reflection coefficients.

The relevant fluxes are

- $v_1|A|^2$
- $v_1|B|^2$
- $v_3|F|^2$

where $v_1 = v_3$.

The reflection coefficient is

$$\begin{aligned}
R &= \frac{v_1}{v_1}\left|\frac{B}{A}\right|^2 \\
&= \left|\frac{B}{A}\right|^2 \\
&= \frac{B^*B}{A^*A} \\
&= \frac{\left(\frac{F^2(\phi^2-k^2)^2 sin^2\phi a}{4k^2\phi^2}\right)}{\frac{F^2}{16k^2\phi^2}[16k^2\phi^2 cos^2\phi a + 4(k^2+\phi^2)^2 sin^2\phi a]} \\
&= \frac{\left[\frac{(\phi^2-k^2)^2 sin^2\phi a}{4}\right]}{\frac{1}{4}[4k^2\phi^2 cos^2\phi a + (k^2+\phi^2)^2 sin^2\phi a]} \\
&= \frac{(\phi^2-k^2)^2 sin^2\phi a}{4k^2\phi^2 cos^2\phi a + (k^2+\phi^2)^2 sin^2\phi a}
\end{aligned}$$

yielding our desired reflection coefficient

$$\boxed{R = \frac{(\phi^2-k^2)^2 sin^2\phi a}{4k^2\phi^2 cos^2\phi a + (k^2+\phi^2)^2 sin^2\phi a}} \tag{16.11}$$

Now we need to find our transmission coefficient.

$$\begin{aligned}
T &= \frac{v_3}{v_1}\left|\frac{F}{A}\right|^2 \\
&= \left|\frac{F}{A}\right|^2 \\
&= \frac{F^*F}{A^*A} \\
&= \frac{F^2}{\left(\frac{F^2}{16k^2\phi^2}\right)[16k^2\phi^2 cos^2\phi a + 4(k^2+\phi^2)^2 sin^2\phi a]} \\
&= \frac{16k^2\phi^2}{16k^2\phi^2 cos^2\phi a + 4(k^2+\phi^2)^2 sin^2\phi a}
\end{aligned}$$

yielding our desired transmission coefficient.

$$\boxed{T = \frac{1}{cos^2\phi a + \frac{(k^2+\phi^2)^2}{4k^2\phi^2} sin^2\phi a}} \tag{16.12}$$

Now you could stop here but in many textbooks they keep going by recognizing that $k^2 = \left(\frac{2m\epsilon}{\hbar^2}\right)$ and $\phi^2 = \left(\frac{2m(\epsilon-V)}{\hbar^2}\right)$. This leads to

$$\boxed{T = \frac{1}{1+\frac{V^2}{4\epsilon(\epsilon-V)}sin^2\phi a}} \tag{16.13}$$

although I won't go through the math to get it.

Case 2 ($\epsilon < V$)

Again, assume a source of particles on the left only. What is the behavior of the wavefunction? What does the transmission $T = \left|\frac{F}{A}\right|^2$ and reflection $R = \left|\frac{B}{A}\right|^2$ coefficients look like? To begin with, we have the following wavefunctions in regions 1, 2, and 3 as

$$\begin{aligned}\Psi_1 &= Ae^{ikx} + Be^{-ikx}\\ \Psi_2 &= Ce^{\phi x} + De^{-\phi x}\\ \Psi_3 &= Fe^{ikx} + Ge^{-ikx}\end{aligned}$$

where $k^2 = \frac{2m\epsilon}{\hbar^2}$ and $\phi^2 = \frac{2m(V-\epsilon)}{\hbar^2}$. Also remember that there is no source of particles on the right. Therefore $G = 0$ above. This leaves

$$\boxed{Ae^{ikx} + Be^{-ikx}}$$
$$\boxed{Ce^{\phi x} + De^{-\phi x}}$$
$$\boxed{Fe^{ikx}}$$

Like in the previous case, we apply matching conditions to merge the wavefunctions at the different interfaces between regions 1, 2, and 3. This gives

$$\begin{gathered}\Psi_1(0) = \Psi_2(0)\\ \Psi_1'(0) = \Psi_2'(0)\\ \Psi_2(a) = \Psi_3(a)\\ \Psi_2'(a) = \Psi_3'(a)\end{gathered}$$

From the first two equations we have

$$\begin{aligned}
A+B &= C+D \\
ikA-ikB &= \phi C-\phi D \\
&\text{or} \\
A+B &= C+D \\
A-B &= \frac{\phi}{ik}C-\frac{\phi}{ik}D \\
&\text{leading to} \\
2A &= \left(1+\frac{\phi}{ik}\right)C+\left(1-\frac{\phi}{ik}\right)D
\end{aligned}$$

or

$$\boxed{A=\tfrac{1}{2}\left(1+\tfrac{\phi}{ik}\right)C+\tfrac{1}{2}\left(1-\tfrac{\phi}{ik}\right)D} \tag{16.14}$$

alternatively we can solve for B

$$2B=\left(1-\frac{\phi}{ik}\right)C+\left(1+\frac{\phi}{ik}\right)D$$

giving

$$\boxed{B=\tfrac{1}{2}\left(1-\tfrac{\phi}{ik}\right)C+\tfrac{1}{2}\left(1+\tfrac{\phi}{ik}\right)D} \tag{16.15}$$

From the second two matching conditions we have

$$\begin{aligned}
Ce^{\phi a}+De^{-\phi a} &= Fe^{ika} \\
\phi Ce^{\phi a}-\phi De^{-\phi a} &= ikFe^{ika} \\
&\text{or} \\
Ce^{\phi a}+De^{-\phi a} &= Fe^{ika} \\
Ce^{\phi a}-De^{-\phi a} &= \frac{ik}{\phi}Fe^{ika} \\
&\text{leading to} \\
2Ce^{\phi a} &= \left(1+\frac{ik}{\phi}\right)Fe^{ika} \\
2C &= \left(1+\frac{ik}{\phi}\right)Fe^{ika}e^{-\phi a}
\end{aligned}$$

giving

$$\boxed{C = \tfrac{1}{2}\left(1 + \tfrac{ik}{\phi}\right) F e^{ika} e^{-\phi a}} \tag{16.16}$$

alternatively we can solve for D

$$\begin{aligned} 2De^{-\phi a} &= \left(1 - \frac{ik}{\phi}\right) F e^{ika} \\ 2D &= \left(1 - \frac{ik}{\phi}\right) F e^{ika} e^{\phi a} \end{aligned}$$

giving

$$\boxed{D = \tfrac{1}{2}\left(1 - \tfrac{ik}{\phi}\right) F e^{ika} e^{\phi a}} \tag{16.17}$$

Now express A and B in terms of F

$$\begin{aligned} A &= \frac{1}{2}\left(1 + \frac{\phi}{ik}\right) C + \frac{1}{2}\left(1 - \frac{\phi}{ik}\right) D \\ &= \frac{1}{2}\left(1 + \frac{\phi}{ik}\right) \frac{1}{2}\left(1 + \frac{ik}{\phi}\right) F e^{ika-\phi a} + \frac{1}{2}\left(1 - \frac{\phi}{ik}\right) \frac{1}{2}\left(1 - \frac{ik}{\phi}\right) F e^{ika+\phi a} \\ &= \frac{Fe^{ika}}{4}\left(1 + \frac{\phi}{ik}\right)\left(1 + \frac{ik}{\phi}\right) e^{-\phi a} + \frac{Fe^{ika}}{4}\left(1 - \frac{\phi}{ik}\right)\left(1 - \frac{ik}{\phi}\right) e^{\phi a} \\ &= \frac{Fe^{ika}}{4}\left[\left(1 + \frac{\phi}{ik}\right)\left(1 + \frac{ik}{\phi}\right) e^{-\phi a} + \left(1 - \frac{\phi}{ik}\right)\left(1 - \frac{ik}{\phi}\right) e^{\phi a}\right] \\ &= \frac{Fe^{ika}}{4}\left[\left(\frac{\phi + ik}{ik}\right)\left(\frac{\phi + ik}{\phi}\right) e^{-\phi a} - \left(\frac{\phi - ik}{ik}\right)\left(\frac{\phi - ik}{\phi}\right) e^{\phi a}\right] \\ &= \frac{Fe^{ika}}{4ik\phi}\left[(\phi + ik)^2 e^{-\phi a} - (\phi - ik)^2 e^{\phi a}\right] \\ &= \frac{Fe^{ika}}{4ik\phi}[(\phi^2 + 2ik\phi - k^2)e^{-\phi a} - (\phi^2 - 2ik\phi - k^2)e^{\phi a}] \\ &= \frac{Fe^{ika}}{4ik\phi}[-\phi^2(-e^{-\phi a} + e^{\phi a}) + 2ik\phi(e^{-\phi a} + e^{\phi a}) + k^2(-e^{-\phi a} + e^{\phi a})] \\ &= \frac{Fe^{ika}}{4ik\phi}[(k^2 - \phi^2)(e^{\phi a} - e^{-\phi a}) + 2ik\phi(e^{\phi a} + e^{-\phi a})] \\ &= \frac{Fe^{ika}}{4ik\phi}[2(k^2 - \phi^2) sinh\phi a + 4ik\phi cosh\phi a] \end{aligned}$$

leaving

$$\boxed{A = \frac{Fe^{ika}}{2ik\phi}[(k^2 - \phi^2)sinh\phi a + 2ik\phi cosh\phi a]} \tag{16.18}$$

We can now evaluate the transmission coefficient.

$$\begin{aligned}
T &= \frac{F^2}{\frac{F^2}{4k^2\phi^2}[(k^2 - \phi^2)^2 sinh^2\phi a + 4k^2\phi^2 cosh^2\phi a]} \\
&= \frac{4k^2\phi^2}{4k^2\phi^2 cosh^2\phi a + (k^2 - \phi^2)^2 sinh^2\phi a} \\
&= \frac{1}{cosh^2\phi a + \frac{(k^2-\phi^2)^2}{4k^2\phi^2} sinh^2\phi a} \\
& \text{where recall that } cosh^2\phi a = 1 + sinh^2\phi a \\
&= \frac{1}{1 + sinh^2\phi a\left(1 + \frac{(k^2-\phi^2)^2}{4k^2\phi^2}\right)} \\
& \text{break up the term in parenthesis. It becomes } (k^2 + \phi^2)^2
\end{aligned}$$

this gives our desired transmission coefficient

$$\boxed{T = \frac{1}{1 + \frac{(k^2+\phi^2)^2}{4k^2\phi^2} sinh^2\phi a}} \tag{16.19}$$

Note that this result is nonzero and hence nonclassical. You can have probability of finding the particle in an energetically forbidden region. This is called tunneling.

Now for the reflection coefficient. Here we need to find B.

$$\begin{aligned}
B &= \frac{1}{2}\left(1-\frac{\phi}{ik}\right)C+\frac{1}{2}\left(\frac{1+\phi}{ik}\right)D \\
&= \frac{1}{2}\left(\frac{1-\phi}{ik}\right)\left[\frac{1}{2}\left(1+\frac{ik}{\phi}\right)Fe^{ika-\phi a}\right]+\frac{1}{2}\left(1+\frac{\phi}{ik}\right)\left[\frac{1}{2}\left(1-\frac{ik}{\phi}\right)Fe^{ika+\phi a}\right] \\
&= \frac{F}{4}\left(1-\frac{\phi}{ik}\right)\left(1+\frac{ik}{\phi}\right)e^{ika-\phi a}+\frac{F}{4}\left(1+\frac{\phi}{ik}\right)\left(1-\frac{ik}{\phi}\right)e^{ika+\phi a} \\
&= \frac{Fe^{ika}}{4}\left(\frac{ik-\phi}{ik}\right)\left(\frac{\phi+ik}{\phi}\right)e^{-\phi a}+\frac{Fe^{ika}}{4}\left(\frac{ik+\phi}{ik}\right)\left(\frac{\phi-ik}{\phi}\right)e^{\phi a} \\
&= \frac{Fe^{ika}}{4ik\phi}\left[-(\phi-ik)(\phi+ik)e^{-\phi a}+(\phi-ik)(\phi+ik)e^{\phi a}\right] \\
&= \frac{Fe^{ika}}{4ik\phi}\left[2(\phi^2+k^2)\frac{(e^{\phi a}-e^{-\phi a})}{2}\right] \\
&= \frac{Fe^{ika}}{2ik\phi}[(\phi^2+k^2)sinh\phi a]
\end{aligned}$$

yielding our desired expression

$$\boxed{B=\tfrac{Fe^{ika}}{2ik\phi}(\phi^2+k^2)sinh\phi a} \tag{16.20}$$

Now put it all together to get the reflection coefficient.

$$\begin{aligned}
R &= \left|\frac{B}{A}\right|^2 \\
&= \frac{\frac{F^2(\phi^2+k^2)^2 sinh^2\phi a}{4k^2\phi^2}}{\frac{F^2[(k^2-\phi^2)^2 sinh^2\phi a+4k^2\phi^2 cosh^2\phi a]}{4k^2\phi^2}} \\
&= \frac{(\phi^2+k^2)^2 sinh^2\phi a}{[(k^2-\phi^2)^2 sinh^2\phi a+4k^2\phi^2 cosh^2\phi a]} \\
&= \frac{(\phi^2+k^2)^2}{(k^2-\phi^2)^2+4k^2\phi^2\frac{cosh^2\phi a}{sinh^2\phi a}}
\end{aligned}$$

where recall that $tanh^2\phi a = \dfrac{cosh^2\phi a}{sinh^2\phi a}$

This gives our desired reflection coefficient

$$\boxed{R=\tfrac{(\phi^2+k^2)^2}{(\phi^2-k^2)^2+4k^2\phi^2 tanh^2\phi a}} \tag{16.21}$$

Chapter 17

Nondegenerate perturbation theory

The basic idea here is that the true Hamiltonian $\hat{H}$ is close to an approximate Hamiltonian $\hat{H}^{(0)}$ whose eigenfunctions and eigenvalues are known. The difference $\hat{H}^{(1)}$ is called a perturbation. Higher order corrections such as $\hat{H}^{(2)}, \hat{H}^{(3)} \ldots$ can be included if desired. Usually though you will stop at the first or second correction to either the energies or wavefunctions.

- We introduce a parameter λ to keep track of the order or alternatively, the order of refinement of the solutions.
- So 1st order corrections from $\hat{H}^{(1)}$ have a λ in front of it.
- 2nd order corrections from $\hat{H}^{(2)}$ will have λ^2 in front of it
- and so on in this fashion
- Also λ does not represent any real physical quantity. It is simply a mathematical technique for keeping track of the order of approximation. In the end we will usually set $\lambda = 1$ but the method is valid for any fraction of λ.

Our corrected Hamiltonian is therefore

$$\hat{H} = \hat{H}^{(0)} + \lambda \hat{H}^{(1)} + \lambda^2 \hat{H}^{(2)} + \ldots$$

where $\hat{H}^{(0)}$ is our unperturbed Hamiltonian whose eigenvalues and eigenvectors we know. Our wavefunctions and energies are

$$\begin{aligned} \Psi &= \Psi^{(0)} + \lambda \Psi^{(1)} + \lambda^2 \Psi^{(2)} + \ldots \\ \epsilon &= \epsilon^{(0)} + \lambda \epsilon^{(1)} + \lambda^2 \epsilon^{(2)} + \ldots \end{aligned}$$

The results of perturbation theory are derived by taking the exact Schrodinger equation $H\Psi = \epsilon\Psi$ and substituting in our above expressions for Ψ and ϵ. Next we group all terms with the same power of λ.

$$\begin{aligned} & [H^{(0)} + \lambda H^{(1)} + \lambda^2 H^{(2)}][\Psi^{(0)} + \lambda\Psi^{(1)} + \lambda^2\Psi^{(2)}] \\ = \; & [\epsilon^{(0)} + \lambda\epsilon^{(1)} + \lambda^2\Psi^{(2)}][\Psi^{(0)} + \lambda\Psi^{(1)} + \lambda^2\Psi^{(2)}] \end{aligned}$$

Ok things get complicated here. We will separately evaluate the left and right hand side of these expressions. In addition, we will consider terms only up to second order (i.e. drop λ^3 and higher terms).

Left hand side

$$\begin{aligned} H^{(0)}\Psi^{(0)} \; + \; & \lambda H^{(0)}\Psi^{(1)} + \lambda^2 H^{(0)}\Psi^{(2)} + \lambda^3 H^{(1)}\Psi^{(2)} + \lambda^4 H^{(2)}\Psi^{(2)} \\ + \; & \lambda H^{(1)}\Psi^{(0)} + \lambda^2 H^{(1)}\Psi^{(1)} + \lambda^3 H^{(2)}\Psi^{(1)} \\ & \qquad + \lambda^2 H^{(2)}\Psi^{(0)} \end{aligned}$$

When we consider terms only up to second order we get

$$H^{(0)}\Psi^{(0)} + \lambda[H^{(0)}\Psi^{(1)} + H^{(1)}\Psi^{(0)}] + \lambda^2[H^{(0)}\Psi^{(2)} + H^{(1)}\Psi^{(1)} + H^{(2)}\Psi^{(0)}]$$

Right hand side

$$\begin{aligned} \epsilon^{(0)}\Psi^{(0)} \; + \; & \lambda\epsilon^{(0)}\Psi^{(1)} + \lambda^2\epsilon^{(0)}\Psi^{(2)} + \lambda^3\epsilon^{(1)}\Psi^{(2)} + \lambda^4\epsilon^{(2)}\Psi^{(2)} \\ + \; & \lambda\epsilon^{(1)}\Psi^{(0)} + \lambda^2\epsilon^{(1)}\Psi^{(1)} + \lambda^3\epsilon^{(2)}\Psi^{(1)} \\ & \qquad + \lambda^2\epsilon^{(2)}\Psi^{(0)} \end{aligned}$$

When we consider terms only up to second order we get

$$\epsilon^{(0)}\Psi^{(0)} + \lambda[\epsilon^{(0)}\Psi^{(1)} + \epsilon^{(1)}\Psi^{(0)}] + \lambda^2[\epsilon^{(0)}\Psi^{(2)} + \epsilon^{(1)}\Psi^{(1)} + \epsilon^{(2)}\Psi^{(0)}]$$

Now because the solution must be true for all values of λ one can equate the coefficients of power of λ giving

$$\boxed{H^{(0)}\Psi^{(0)} = \epsilon^{(0)}\Psi^{(0)}}$$

$$\boxed{H^{(0)}\Psi^{(1)} + H^{(1)}\Psi^{(0)} = \epsilon^{(0)}\Psi^{(1)} + \epsilon^{(1)}\Psi^{(0)}}$$

$$\boxed{H^{(0)}\Psi^{(2)} + H^{(1)}\Psi^{(1)} + H^{(2)}\Psi^{(0)} = \epsilon^{(0)}\Psi^{(2)} + \epsilon^{(1)}\Psi^{(1)} + \epsilon^{(2)}\Psi^{(0)}}$$

Let's rearrange these expressions to get

$$\boxed{(H^{(0)}-\epsilon^{(0)})\Psi^{(0)}=0} \tag{17.1}$$

$$\boxed{(H^{(0)}-\epsilon^{(0)})\Psi^{(1)}+(H^{(1)}-\epsilon^{(1)})\Psi^{(0)}=0} \tag{17.2}$$

$$\boxed{(H^{(0)}-\epsilon^{(0)})\Psi^{(2)}+(H^{(1)}-\epsilon^{(1)})\Psi^{(1)}+(H^{(2)}-\epsilon^{(2)})\Psi^{(0)}=0} \tag{17.3}$$

The first of the three equations is our unperturbed case. It provides our zero-order solutions. Nothing special here.

Now multiply all expression by $\Psi^{*(0)}$ and integrate. Also let's switch to bra-ket notation so I don't have to write out the integrals.

$$\begin{aligned}
<\Psi^{(0)}|H^{(0)}-\epsilon^{(0)}|\Psi^{(0)}> &= 0\\
<\Psi^{(0)}|H^{(0)}-\epsilon^{(0)}|\Psi^{(1)}>+<\Psi^{(0)}|H^{(1)}-\epsilon^{(1)}|\Psi^{(0)}> &= 0\\
<\Psi^{(0)}|H^{(0)}-\epsilon^{(0)}|\Psi^{(2)}>+<\Psi^{(0)}|H^{(1)}-\epsilon^{(1)}|\Psi^{(1)}>+<\Psi^{(0)}|H^{(2)}-\epsilon^{(2)}|\Psi^{(0)}> &= 0
\end{aligned}$$

Now in the case of the first order and second order expressions the first term in each case is zero.

$$\begin{aligned}
<\Psi^{(0)}|H^{(0)}-\epsilon^{(0)}|\Psi^{(1)}> &= 0\\
<\Psi^{(0)}|H^{(0)}-\epsilon^{(0)}|\Psi^{(2)}> &= 0
\end{aligned}$$

this is because $H^{(0)}$ is Hermitian $H^{(0)}=H^{\dagger(0)}$. So you can operate with $H^{(0)}$ on the bra and see that each expression will die. Alternatively, you could also invoke the orthogonality of $<\Psi^{(0)}|$ and $|\Psi^{(1)}>$ after operating on the bra.

This leaves

$$\begin{aligned}
<\Psi^{(0)}|H^{(1)}-\epsilon^{(1)}|\Psi^{(0)}> &= 0 \text{ 1st order}\\
<\Psi^{(0)}|H^{(1)}-\epsilon^{(1)}|\Psi^{(1)}>+<\Psi^{(0)}|H^{(2)}-\epsilon^{(2)}|\Psi^{(0)}> &= 0 \text{ 2nd order}
\end{aligned}$$

Next let's break each expression up and drop any zero terms. We get

$$\begin{aligned}
<\Psi^{(0)}|H^{(1)}|\Psi^{(0)}>-\epsilon^{(1)}<\Psi^{(0)}|\Psi^{(0)}> &= 0\\
<\Psi^{(0)}|H^{(1)}|\Psi^{(1)}>-\epsilon^{(1)}<\Psi^{(0)}|\Psi^{(1)}>+<\Psi^{(0)}|H^{(2)}|\Psi^{(0)}>-\epsilon^{(2)}<\Psi^{(0)}|\Psi^{(0)}> &= 0\\
\text{reducing to}\\
<\Psi^{(0)}|H^{(1)}|\Psi^{(0)}>-\epsilon^{(1)} &= 0\\
<\Psi^{(0)}|H^{(1)}|\Psi^{(1)}>+<\Psi^{(0)}|H^{(2)}|\Psi^{(0)}>-\epsilon^{(2)} &= 0\\
\text{finally simplifying to}\\
<\Psi^{(0)}|H^{(1)}|\Psi^{(0)}> &= \epsilon^{(1)}\\
<\Psi^{(0)}|H^{(1)}|\Psi^{(1)}>+<\Psi^{(0)}|H^{(2)}|\Psi^{(0)}> &= \epsilon^{(2)}
\end{aligned}$$

Therefore for the energies we have the following first and second order corrections to the zero order solutions.

$$\boxed{\epsilon^{(1)} =< \Psi^{(0)}|H^{(1)}|\Psi^{(0)} >} \tag{17.4}$$

$$\boxed{\epsilon^{(2)} =< \Psi^{(0)}|H^{(1)}|\Psi^{(1)} > + < \Psi^{(0)}|H^{(2)}|\Psi^{(2)} >} \tag{17.5}$$

Note that to get the second order energy correction you already need to know what $|\Psi^{(1)} >$ is. The same applies to higher order corrections and means that this can get pretty tedious. Usually you stop at first order corrections. So right now our second order expression is not necessarily in a useful form. We will revisit this later after finding out what $|\Psi^{(1)} >$ looks like.

Example 1, expression for ϵ^3

Please calculate the expression for the third order correction ϵ^3

$$\begin{aligned} H &= H^{(0)} + \lambda H^{(1)} + \lambda^2 H^{(2)} + \lambda^3 H^{(3)} + \ldots \\ \Psi &= \Psi^{(0)} + \lambda \Psi^{(1)} + \lambda^2 \Psi^{(2)} + \lambda^3 \Psi^{(3)} + \ldots \\ \epsilon &= \epsilon^{(0)} + \lambda \epsilon^{(1)} + \lambda^2 \epsilon^{(2)} + \lambda^3 \epsilon^{(3)} + \ldots \end{aligned}$$

Plugging this into the Schrodinger equation we get

$$\begin{aligned} & [H^{(0)} + \lambda H^{(1)} + \lambda^2 H^{(2)} + \lambda^3 H^{(3)}][\Psi^{(0)} + \lambda \Psi^{(1)} + \lambda^2 \Psi^{(2)} + \lambda^3 \Psi^{(3)}] \\ = \; & [\epsilon^{(0)} + \lambda \epsilon^{(1)} + \lambda^2 \epsilon^{(2)} + \lambda^3 \epsilon^{(3)}][\Psi^{(0)} + \lambda \Psi^{(1)} + \lambda^2 \Psi^{(2)} + \lambda^3 \Psi^{(3)}] \end{aligned}$$

Again, since this gets a little involved we will consider the left and right hand side of this equation separately.

Left hand side

$$\begin{aligned} H^{(0)}\Psi^{(0)} &+ \lambda H^{(0)}\Psi^{(1)} + \lambda^2 H^{(0)}\Psi^{(2)} + \lambda^3 H^{(0)}\Psi^{(3)} + \lambda^4 H^{(1)}\Psi^{(3)} \\ &+ \lambda^5 H^{(2)}\Psi^{(3)} + \lambda^6 H^{(3)}\Psi^{(3)} \\ &+ \lambda H^{(1)}\Psi^{(0)} + \lambda^2 H^{(1)}\Psi^{(1)} + \lambda^3 H^{(1)}\Psi^{(2)} + \lambda^4 H^{(2)}\Psi^{(2)} \\ &+ \lambda^5 H^{(3)}\Psi^{(2)} \\ &+ \lambda^2 H^{(2)}\Psi^{(0)} + \lambda^3 H^{(2)}\Psi^{(1)} + \lambda^4 H^{(3)}\Psi^{(1)} \\ &+ \lambda^3 H^{(3)}\Psi^{(0)} \end{aligned}$$

We want the third order corrections here.

Right hand side

$$\begin{aligned}\epsilon^{(0)}\Psi^{(0)} &+ \lambda\epsilon^{(0)}\Psi^{(1)} + \lambda^2\epsilon^{(0)}\Psi^{(2)} + \lambda^3\epsilon^{(0)}\Psi^{(3)} + \lambda^4\epsilon^{(1)}\Psi^{(3)} + \lambda^5\epsilon^{(2)}\Psi^{(3)} + \lambda^6\epsilon^{(3)}\Psi^{(3)} \\ &+ \lambda\epsilon^{(1)}\Psi^{(0)} + \lambda^2\epsilon^{(1)}\Psi^{(1)} + \lambda^3\epsilon^{(1)}\Psi^{(2)} + \lambda^4\epsilon^{(2)}\Psi^{(2)} + \lambda^5\epsilon^{(3)}\Psi^{(2)} \\ &+ \lambda^2\epsilon^{(2)}\Psi^{(0)} + \lambda^3\epsilon^{(2)}\Psi^{(1)} + \lambda^4\epsilon^{(3)}\Psi^{(1)} \\ &+ \lambda^3\epsilon^{(3)}\Psi^{(0)}\end{aligned}$$

We only want the 3rd order corrections here.

This leaves

$$\boxed{H^{(0)}\Psi^{(3)} + H^{(1)}\Psi^{(2)} + H^{(2)}\Psi^{(1)} + H^{(3)}\Psi^{(0)} = \epsilon^{(0)}\Psi^{(3)} + \epsilon^{(1)}\Psi^{(2)} + \epsilon^{(2)}\Psi^{(1)} + \epsilon^{(3)}\Psi^{(0)}}$$

Multiply both sides by $\Psi^{*(0)}$ and integrate. Switching to the Dirac bra-ket notation we get

$$(H^{(0)} - \epsilon^{(0)})|\Psi^{(3)} > +(H^{(1)} - \epsilon^{(1)})|\Psi^{(2)} > +(H^{(2)} - \epsilon^{(2)})|\Psi^{(1)} > +(H^{(3)} - \epsilon^{(3)})|\Psi^{(0)} >= 0$$

$$\begin{aligned} & < \Psi^{(0)}|H^{(0)} - \epsilon^{(0)}|\Psi^{(3)} > + < \Psi^{(0)}|H^{(1)} - \epsilon^{(1)}|\Psi^{(2)} > \\ + & < \Psi^{(0)}|H^{(2)} - \epsilon^{(2)}|\Psi^{(1)} > + < \Psi^{(0)}|H^{(3)-\epsilon^{(3)}}|\Psi^{(0)} >= 0 \\ & \text{the first term drops out leaving} \\ & < \Psi^{(0)}|H^{(1)} - \epsilon^{(1)}|\Psi^{(2)} > + < \Psi^{(0)}|H^{(2)} - \epsilon^{(2)}|\Psi^{(1)} > \\ + & < \Psi^{(0)}|H^{(3)} - \epsilon^{(3)}|\Psi^{(0)} >= 0 \\ & \text{becoming} \\ & < \Psi^{(0)}|H^{(1)}|\Psi^{(2)} > -\epsilon^{(1)} < \Psi^{(0)}|\Psi^{(2)} > + < \Psi^{(0)}|H^{(2)}|\Psi^{(1)} > -\epsilon^{(2)} < \Psi^{(0)}|\Psi^{(1)} > \\ + & < \Psi^{(0)}|H^{(3)}|\Psi^{(0)} > -\epsilon^{(3)} < \Psi^{(0)}|\Psi^{(0)} >= 0 \\ & \text{by orthonormality a bunch of terms drop out giving} \\ & < \Psi^{(0)}|H^{(1)}|\Psi^{(2)} > + < \Psi^{(0)}|H^{(2)}|\Psi^{(1)} > \\ + & < \Psi^{(0)}|H^{(3)}|\Psi^{(0)} >= \epsilon^{(3)}\end{aligned}$$

Therefore our desired 3rd order correction is

$$\boxed{\epsilon^{(3)} =< \Psi^{(0)}|H^{(1)}|\Psi^{(2)} > + < \Psi^{(0)}|H^{(2)}|\Psi^{(1)} > + < \Psi^{(0)}|H^{(3)}|\Psi^{(0)} >} \tag{17.6}$$

Example 2, Particle in a slanted box

We have a particle in a 1D box with a slanted bottom. The perturbation term is $H^{(1)} = \frac{V}{a}x$ where V is some constant. The zeroth order wavefunction is $\Psi^{(0)} = \sqrt{\frac{2}{a}} sin\frac{n\pi x}{a}$ and the zeroth orther energies are $\epsilon^{(0)} = \frac{n^2h^2}{8ma^2}$.

What is the 1st order correction to $\epsilon^{(0)}$?

From nondegenerate perturbation theory the first order correction is

$$\begin{aligned}
\epsilon^{(1)} &= <\psi^{(0)}|H^{(1)}|\Psi^{(0)}> \\
&= \int_0^a \left(\sqrt{\frac{2}{a}} sin\frac{n\pi x}{a}\right)\left(\frac{V}{a}x\right)\left(\sqrt{\frac{2}{a}} sin\frac{n\pi x}{a}\right) dx \\
&= \frac{2}{a}\left(\frac{V}{a}\right)\int_0^a x sin^2\frac{n\pi x}{a} dx \\
& \text{let } b = \frac{n\pi}{a} \\
&= \frac{2V}{a^2}\int_0^a x sin^2 bx dx \\
& \text{where } sin^2 bx = \frac{1}{2}(1 - cos2bx) \\
&= \frac{2V}{a^2}\left[\frac{1}{2}\int_0^a x(1 - cos2bx)dx\right] \\
&= \frac{V}{a^2}\left[\int_0^a x dx - \int_0^a x cos2bx dx\right] \\
&= \frac{V}{a^2}\left[\frac{x^2}{2}|_0^a - \int_0^a x cos2bx dx\right] \\
&= \frac{V}{a^2}\left[\frac{a^2}{2} - \int_0^a x cos2bx dx\right]
\end{aligned}$$

Solve the integral by parts. Let $u = x, du = dx, dv = cos2bxdx, v = \frac{1}{2b}sin2bx$. We get

$$\begin{aligned}
&= \frac{V}{2} - \frac{V}{a^2}\left[\frac{x}{2b}sin2bx|_0^a - \int_0^a \frac{1}{2b}sin2bx dx\right] \\
&= \frac{V}{2} - \frac{V}{a^2}\left[\frac{x}{2b}sin2bx|_0^a + \frac{1}{2b}\frac{1}{2b}cos2bx|_0^a\right] \\
& \text{the first term is zero} \\
&= \frac{V}{2} - \frac{V}{a^2}\left[\frac{1}{4b^2}cos2bx|_0^a\right] \\
& \text{the term in brackets is also zero}
\end{aligned}$$

therefore

$$\boxed{\epsilon^{(1)} = \frac{V}{2}} \tag{17.7}$$

This is our desired 1st order correction.

The final corrected energies are then

$$\boxed{\epsilon = \frac{n^2h^2}{8ma^2} + \frac{V}{2}} \tag{17.8}$$

where $n = 1, 2, 3, \ldots$

Example 3, An anharmonic oscillator

Consider an anharmonic oscillator whose potential is $U(x) = \frac{1}{2}kx^2 + \frac{1}{6}\gamma x^3$. Note that this problem does not require a lot of math.

Calculate the 1st order correction to the ground state energy. We have

$$\begin{aligned} \epsilon &= (n + \frac{1}{2})h\nu \\ \Psi &= N_n H_n(\alpha^{\frac{1}{2}}x)e^{-\frac{\alpha x^2}{2}} \end{aligned}$$

where $\alpha = \sqrt{\frac{k\mu}{\hbar^2}}$ and the normalization constant is $N_n = \frac{1}{\sqrt{2^n n!}}\left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}}$

The first order energy correction is

$$\epsilon^{(1)} =< \Psi^{(0)}|H^{(1)}|\Psi^{(0)} >$$

where $H^{(1)} = \frac{1}{6}\gamma x^3$. We have

$$\begin{aligned} &= \frac{\gamma}{6}\int_{-\infty}^{\infty}\left(N_n H_n(\alpha^{\frac{1}{2}}x)e^{-\frac{\alpha x^2}{2}}\right)(x^3)\left(N_n H_n(\alpha^{\frac{1}{2}}x)e^{-\frac{\alpha x^2}{2}}\right)dx \\ &= \frac{\gamma}{6}N_n^2\int_{-\infty}^{\infty}[H_n(\alpha^{\frac{1}{2}}x)][x^3][H_n(\alpha^{\frac{1}{2}}x)]e^{-\alpha x^2}dx \end{aligned}$$

Now if $n = 0$ $H_0(\alpha^{\frac{1}{2}}x) = 1$ leaving

$$= \frac{\gamma}{6}N_n^2\int_{-\infty}^{\infty}x^3e^{-\alpha x^2}dx$$

The first term in the integral is odd. The second is even. Now by symmetry their product is overall odd and over the range of the integral it evaluates to zero. Therefore

$$\boxed{\epsilon^{(1)} = 0} \tag{17.9}$$

This is our desired first order correction. So to first order the overall energies are

$$\boxed{\epsilon = (n + \tfrac{1}{2})h\nu} \tag{17.10}$$

Example 4, Another anharmonic oscillator

Calculate the 1st order correction to the ground state energy of an anharmonic oscillator whose potential energy is

$$\begin{aligned} U(x) &= \frac{1}{2}kx^2 + \frac{1}{6}\gamma x^3 + \frac{1}{24}bx^4 \\ H^{(1)} &= \frac{1}{6}\gamma x^3 + \frac{1}{24}bx^4 \\ \epsilon &= (n + \frac{1}{2})h\nu \\ \Psi &= N_n H_n(\alpha^{\frac{1}{2}}x)e^{-\frac{\alpha x^2}{2}} \end{aligned}$$

where $\alpha = \sqrt{\frac{k\mu}{\hbar^2}}$ and the normalization constant is $N = \frac{1}{\sqrt{2^n n!}}\left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}}$ and $N_0 = \left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}}$ if $n = 0$. The first order energy correction is

$$\begin{aligned} \epsilon^{(1)} &= < \Psi^{(0)}|H^{(1)}|\Psi^{(0)} > \\ &= \int_{-\infty}^{\infty} \left(N_0 H_0(\alpha^{\frac{1}{2}}x)e^{-\frac{\alpha x^2}{2}}\right)\left(\frac{1}{6}\gamma x^3 + \frac{1}{24}bx^4\right)\left(N_0 H_0(\alpha^{\frac{1}{2}}x)e^{-\frac{\alpha x^2}{2}}\right) dx \end{aligned}$$

We have already done the 1st term. By symmetry it drops out leaving.

$$\begin{aligned} &= \frac{b}{24}N_0^2 \int_{-\infty}^{\infty} (H_0(\alpha^{\frac{1}{2}}x))(x^4)(H_0(\alpha^{\frac{1}{2}}x))e^{-\alpha x^2} dx \\ &\quad \text{where } H_0(\alpha^{\frac{1}{2}}x) = 1 \\ &= \frac{b}{24}N_0^2 \int_{-\infty}^{\infty} x^4 e^{-\alpha x^2} dx \\ &\quad \text{this integral does not dissapear by symmetry} \\ &\quad \text{and must be evaluated} \\ &= \frac{bN_0^2}{12} \int_{-\infty}^{\infty} x^4 e^{-\alpha x^2} dx \\ &\quad \text{looking this up in a table of integrals} \end{aligned}$$

where

$$\boxed{\int_0^{\infty} x^{2n} e^{-\alpha x^2} dx = \frac{1{\cdot}3{\cdot}5{\cdot}(2n-1)}{2^{n+1}\alpha^n}\sqrt{\frac{\pi}{\alpha}}}$$

Our integral evaluates to $\frac{3}{8\alpha^2}\sqrt{\frac{\pi}{\alpha}}$. The expression becomes

$$
\begin{aligned}
&= \frac{bN_0^2}{12}\left(\frac{3}{8\alpha^2}\right)\sqrt{\frac{\pi}{\alpha}} \\
&= \frac{bN_0^2}{32\alpha^2}\sqrt{\frac{\pi}{\alpha}} \\
&\quad \text{where } N_0^2 = \sqrt{\frac{\alpha}{\pi}} \text{ giving} \\
&= \frac{b}{32\alpha^2} \\
&\quad \text{where } \alpha^2 = \frac{k\mu}{\hbar^2} \text{ giving} \\
&= \frac{b\hbar^2}{32k\mu}
\end{aligned}
$$

The overall energy with the first order correction is therefore

$$\epsilon = (n + \frac{1}{2})h\nu + \frac{b\hbar^2}{32k\mu}$$

$$\boxed{\epsilon = \left(n + \tfrac{1}{2}\right) + h\nu + \tfrac{b\hbar^2}{32k\mu}} \tag{17.11}$$

Wavefunctions

Now that we have the energy corrections, what about the wavefunctions? Note that you will usually go to second order in the energies but only 1st order in the wavefunctions. Note that this is also called the Raleigh Ritz method.

We have $\Psi_i^{(0)}$ which is our unperturbed wavefunction. We know that we have corrections like

$$\Psi_{tot} = \Psi_i^{(0)} + \lambda\Psi_i^{(1)} + \lambda^2\Psi_i^{(2)} + \dots$$

A convenient way to express $\Psi^{(1)}$ is as a linear expansion in unperturbed wavefunctions which we will denote as $\Psi_j^{(0)}$ or $|j>$. We then have

$$\Psi_i^{(1)} = \sum_j c_{ij}|j>$$

and where c_{ij} are weights representing how much of each unperturbed wavefunction is present.

If we go back to our expression where we derived the 1st order corrections in energy we have

$$\begin{aligned}(H^{(0)}-\epsilon_i^{(0)})\Psi_i^{(1)}+(H^{(1)}-\epsilon_i^{(1)})\Psi_i^{(0)} &= 0\\ H^{(0)}\Psi_i^{(1)}+H^{(1)}\Psi_i^{(0)} &= \epsilon_i^{(0)}\Psi_i^{(1)}+\epsilon_i^{(1)}\Psi_i^{(0)}\end{aligned}$$

Now recall that $\Psi_i^{(1)}=\sum_j c_{ij}|j>$ and replace into the above expression

$$\begin{aligned}H^{(0)}\sum_j c_{ij}|j>+H^{(1)}|i> &= \epsilon_i^{(0)}\sum_j c_{ij}|j>+\epsilon_i^{(1)}|i>\\ \sum_j c_{ij}H^{(0)}|j>+H^{(1)}|i> &= \epsilon_i^{(0)}\sum_j c_{ij}|j>+\epsilon_i^{(1)}|i>\end{aligned}$$

Recall that $|j>$ are eigenfunctions of $H^{(0)}$ since we expanded in the unperturbed basis.

$$\begin{aligned}\sum_j c_{ij}\epsilon_j^{(0)}|j>+H^{(1)}|i> &= \epsilon_i^{(0)}\sum_j c_{ij}|j>+\epsilon_i^{(1)}|i>\\ \epsilon_j^{(0)}\sum_j c_{ij}|j>+H^{(1)}|i> &= \epsilon_i^{(0)}\sum_j c_{ij}|j>+\epsilon_i^{(1)}|i>\end{aligned}$$

Next to start finding our desired coefficients c_{ij} multiply both sides by $<k|$ which is a member of the unperturbed basis. Note that $k\neq i$.

$$\begin{aligned}\epsilon_j^{(0)}\sum_j c_{ij}<k|j>+<k|H^{(1)}|i> &= \epsilon_i^{(0)}\sum_j c_{ij}<k|j>+\epsilon_i^{(1)}<k|i>\\ \epsilon_j^{(0)}\sum_j c_{ij}<k|j>+<k|H^{(1)}|i> &= \epsilon_i^{(0)}\sum_j c_{ij}<k|j>\end{aligned}$$

Now due to the orthogonality between $|k>$ and $|j>$ the only terms in the above expression that survive are those where $k=j$.

$$\epsilon_k^{(0)}\sum_k cik+<k|H^{(1)}|i> \;=\; \epsilon_i^{(0)}\sum_k c_{ik}$$

Consolidate our desired c_{ik} terms to get

$$\sum_k c_{ik}(\epsilon_k^{(0)}-\epsilon_i^{(0)})=-<k|H^{(1)}|i>$$

Therefore

$$c_{ik} = -\frac{< k|H^{(1)}|i >}{(\epsilon_k^{(0)} - \epsilon_i^{(0)})}$$

$$\boxed{c_{ik} = \frac{<k|H^{(1)}|i>}{(\epsilon_i^{(0)} - \epsilon_k^{(0)})}} \tag{17.12}$$

These are our desired correction coefficients. Also recall that $\Psi^{(1)} = \sum_j c_{ij}|j>$ so you can see that the corrected wavefunction to first order is

$$\boxed{|\Psi >= |i > + \sum_k \frac{<k|H^{(1)}|i>}{(\epsilon_i^{(0)} - \epsilon_k^{(0)})}|k >} \tag{17.13}$$

The correction is

$$\boxed{\Psi^{(1)} = \sum_k \frac{<k|H^{(1)}|i>}{(\epsilon_i^{(0)} - \epsilon_k^{(0)})}|k >} \tag{17.14}$$

Now that we have the 1st order correction to the wavefunction, we can go back and express the 2nd order correction in energy in a more useful form.

Recall that

$$\epsilon^{(2)} =< \Psi_i^{(0)}|H^{(1)}|\Psi_i^{(1)} > + < \Psi_i^{(0)}|H^{(2)}|\Psi_i^{(0)} >$$

where we didn't know $|\Psi_i^{(1)} >$ before. Now that we have an explicit form we can substitute it in. To make life even easier assume that the total perturbation goes only to first order, thus $H^{(2)} = 0$. We get

$$\begin{aligned}\epsilon^{(2)} &= < \Psi_i^{(0)}|H^{(1)}|\Psi_i^{(1)} > \\ &= \sum_k \frac{< k|H^{(1)}|i >< i|H^{(1)}|k >}{(\epsilon_i^{(0)} - \epsilon_k^{(0)})}\end{aligned}$$

The final expression is

$$\boxed{\epsilon^{(2)} = \sum_k \frac{<k|H^{(1)}|i><i|H^{(1)}|k>}{(\epsilon_i^{(0)} - \epsilon_k^{(0)})}} \tag{17.15}$$

This is a more user friendly 2nd order energy correction. Also note that $i \neq k$. This is called non-degenerate perturbation theory.

Summary

$$\boxed{\epsilon^{(1)} =< i|H^{(1)}|i >} \tag{17.16}$$

$$\boxed{\epsilon^{(2)} = \sum_k \frac{<k|H^{(1)}|i><i|H^{(1)}|k>}{(\epsilon_i^{(0)}-\epsilon_k^{(0)})} = \sum_k \frac{|<k|H^{(1)}|i>|^2}{(\epsilon_i^{(0)}-\epsilon_k^{(0)})}} \tag{17.17}$$

$$\boxed{|\Psi >= |i > + \sum_k \frac{<k|H^{(1)}|i>}{(\epsilon_i^{(0)}-\epsilon_k^{(0)})}|k >} \tag{17.18}$$

So you see that we will typically go to second order corrections in the energies and only to 1st order in the wavefunctions.

What about 3rd order corrections?

Going back for the 3rd order non-degenerate energy correction $\epsilon^{(3)}$. Here is an alternative expression where we don't need to know $|\Psi_i^{(2)} >$ only $|\Psi_i^{(1)} >$.

Starting with

$$\epsilon_i^{(3)} =< \Psi_i^{(0)}|H^{(1)}|\Psi_i^{(2)} > + < \Psi_i^{(0)}|H^{(2)}|\Psi_i^{(1)} > + < \Psi_i^{(0)}|H^{(3)}|\Psi_i^{(0)} >$$

and with

$$\begin{aligned}(H^{(0)} - \epsilon_i^{(0)})\Psi_i^{(1)} + (H^{(1)} - \epsilon_i^{(1)})\Psi_i^{(0)} &= 0\\ (H^{(0)} - \epsilon_i^{(0)})\Psi_i^{(2)} + (H^{(1)} - \epsilon_i^{(1)})\Psi_i^{(1)} + (H^{(2)} - \epsilon_i^{(2)})\Psi_i^{(0)} &= 0\end{aligned}$$

Using the second and third equations we will try and get rid of the first term in the first equation. To do this, multiply the second expression by $\Psi^{*(2)}$ and integrate. Multiply the third expression by $\Psi^{*(1)}$ and integrate.

Second expression

From the second expression we get the following

$$\begin{aligned}\Psi^{*(2)}(H^{(0)} - \epsilon_i^{(0)})\Psi_i^{(1)} + \Psi_i^{*(2)}(H^{(1)} - \epsilon_i^{(1)})\Psi_i^{(0)} &= 0\\ < \Psi_i^{(2)}|H^{(0)} - \epsilon_i^{(0)}|\Psi_i^{(1)} > + < \Psi_i^{(2)}|H^{(1)} - \epsilon_i^{(1)}|\Psi_i^{(0)} > &= 0\end{aligned}$$

giving

$$\boxed{< \Psi_i^{(2)}|H^{(1)} - \epsilon_i^{(1)}|\Psi_i^{(0)} >= - < \Psi_i^{(2)}|H^{(0)} - \epsilon_i^{(0)}|\Psi_i^{(1)} >}$$

where since $H^{(1)}$ and $H^{(0)}$ and $\epsilon_i^{(1)}$ and $\epsilon_i^{(0)}$ are all Hermitian.

$$\begin{aligned} <\Psi_i^{(0)}|H^{(1)}-\epsilon_i^{(1)}|\Psi_i^{(2)}> &= -<\Psi_i^{(1)}|H^{(0)}-\epsilon_i^{(0)}|\Psi_i^{(2)}> \\ <\Psi_i^{(0)}|H^{(1)}|\Psi_i^{(2)}> &= -<\Psi_i^{(1)}|H^{(0)}-\epsilon_i^{(0)}|\Psi_i^{(2)}> \end{aligned}$$

therefore

$$\epsilon_i^{(3)} = -<\Psi_i^{(1)}|H^{(0)}-\epsilon_i^{(0)}|\Psi_i^{(2)}> + <\Psi_i^{(0)}|H^{(2)}|\Psi_i^{(1)}> + <\Psi_i^{(0)}|H^{(3)}|\Psi_i^{(0)}>$$

Third expression

Now from the third expression we get

$$\begin{aligned} \Psi^{*(1)}(H^{(0)}-\epsilon_i^{(0)})\Psi_i^{(2)} + \Psi^{*(1)}(H^{(1)}-\epsilon_i^{(1)})\Psi_i^{(1)} + \Psi^{*(1)}(H^{(2)}-\epsilon_i^{(2)})\Psi_i^{(0)} &= 0 \\ <\Psi_i^{(1)}|H^{(0)}-\epsilon_i^{(0)}|\Psi_i^{(2)}> + <\Psi_i^{(1)}|H^{(1)}-\epsilon_i^{(1)}|\Psi_i^{(1)}> + <\Psi_i^{(1)}|H^{(2)}-\epsilon_i^{(2)}|\Psi_i^{(0)}> &= 0 \\ &\text{or} \end{aligned}$$

$$-<\Psi_i^{(1)}|H^{(0)}-\epsilon_i^{(0)}|\Psi_i^{(2)}> = <\Psi_i^{(1)}|H^{(1)}-\epsilon_i^{(1)}|\Psi_i^{(1)}> + <\Psi_i^{(1)}|H^{(2)}-\epsilon_i^{(2)}|\Psi_i^{(0)}>$$

Finally using this last expression we can replace it into the result from the second expression above to get

$$\begin{aligned} \epsilon_i^{(3)} &= -<\Psi_i^{(1)}|H^{(0)}-\epsilon_i^{(0)}|\Psi_i^{(2)}> + <\Psi_i^{(0)}|H^{(2)}|\Psi_i^{(1)}> + <\Psi_i^{(0)}|H^{(3)}|\Psi_i^{(0)}> \\ &= [<\Psi_i^{(1)}|H^{(1)}-\epsilon_i^{(1)}|\Psi_i^{(1)}> + <\Psi_i^{(1)}|H^{(2)}-\epsilon_i^{(2)}|\Psi_i^{(0)}>] \\ &+ <\Psi_i^{(0)}|H^{(2)}|\Psi_i^{(1)}> + <\Psi_i^{(0)}|H^{(3)}|\Psi_i^{(0)}> \end{aligned}$$

The only term that simplifies is the second one in brackets. It reduces to $<\Psi_i^{(1)}|H^{(2)}|\Psi_i^{(0)}>$ since $|\Psi_i^{(1)}>$ and $|\Psi_i^{(0)}>$ are orthogonal. Now we get for the 3rd order correction

$$\epsilon_i^{(3)} = <\Psi_i^{(1)}|H^{(1)}-\epsilon_i^{(1)}|\Psi_i^{(1)}> + <\Psi_i^{(1)}|H^{(2)}|\Psi_i^{(0)}> + <\Psi_i^{(0)}|H^{(2)}|\Psi_i^{(1)}> + <\Psi_i^{(0)}|H^{(3)}|\Psi_i^{(0)}>$$

It is apparent that all we need to know now is $|\Psi_i^{(1)}>$

Using

$$\begin{aligned} |\Psi_i^{(1)}> &= \sum_k \frac{<k|H^{(1)}|i>}{(\epsilon_i^{(0)}-\epsilon_k^{(0)})}|k> \\ <\Psi_i^{(1)}| &= \sum_j \frac{<i|H^{(1)}|j>}{(\epsilon_i^{(0)}-\epsilon_j^{(0)})}<j| \end{aligned}$$

Now assume (to make life simple) that the Hamiltonian only has a first order perturbation $H^{(2)} = 0$ and $H^{(3)} = 0$. This leaves behind

$$
\begin{aligned}
\epsilon_i^{(3)} &= <\Psi_i^{(1)}|H^{(1)} - \epsilon_i^{(1)}|\Psi_i^{(1)}> \\
&= <\Psi_i^{(1)}|H^{(1)}|\Psi_i^{(1)}> - <\Psi_i^{(1)}|\epsilon_i^{(1)}|\Psi_i^{(1)}> \\
&= <\Psi_i^{(1)}|H^{(1)}|\Psi_i^{(1)}> - \epsilon_i^{(1)} <\Psi_i^{(1)}|\Psi_i^{(1)}> \\
&= \left[\sum_j \frac{<i|H^{(1)}|j>}{<j|}\right] H^{(1)} \left[\sum_k \frac{<k|H^{(1)}|i>}{(\epsilon_i^{(0)} - \epsilon_k^{(0)})}|k>\right] - \epsilon_i^{(1)} <\Psi_i^{(1)}|\Psi_i^{(1)}> \\
&= \sum_{kj\neq i} \frac{<i|H^{(1)}|j><j|H^{(1)}|k><k|H^{(1)}|i>}{(\epsilon_i^{(0)} - \epsilon_j^{(0)})(\epsilon_i^{(0)} - \epsilon_k^{(0)})} - \epsilon_i^{(1)} <\Psi_i^{(1)}|\Psi_i^{(1)}> \\
&= \sum_{kj\neq i} \frac{<i|H^{(1)}|j><j|H^{(1)}|k><k|H^{(1)}|i>}{(\epsilon_i^{(0)} - \epsilon_j^{(0)})(\epsilon_i^{(0)} - \epsilon_k^{(0)})} \\
&- \epsilon_i^{(1)} \left[\sum_j \frac{<i|H^{(1)}|j>}{(\epsilon_i^{(0)} - \epsilon_j^{(0)})} <j|\right] \left[\sum_k \frac{<k|H^{(1)}|i>}{(\epsilon_i^{(0)} - \epsilon_k^{(0)})}|k>\right] \\
&= \sum_{kj\neq i} \frac{<i|H^{(1)}|j><j|H^{(1)}|k><k|H^{(1)}|i>}{(\epsilon_i^{(0)} - \epsilon_j^{(0)})(\epsilon_i^{(0)} - \epsilon_k^{(0)})} \\
&- \epsilon_i^{(1)} \sum_{kj\neq i} \frac{<i|H^{(1)}|j><j|k><k|H^{(1)}|i>}{(\epsilon_i^{(0)} - \epsilon_j^{(0)})(\epsilon_i^{(0)} - \epsilon_k^{(0)})}
\end{aligned}
$$

Now since we have $<j|k>$ the only terms that are non-zero are those where $j = k$

$$
= \sum_{kj\neq i} \frac{<i|H^{(1)}|j><j|H^{(1)}|k><k|H^{(1)}|i>}{(\epsilon_i^{(0)} - \epsilon_j^{(0)})(\epsilon_i^{(0)} - \epsilon_k^{(0)})} - \epsilon_i^{(1)} \sum_{k\neq i} \frac{<i|H^{(1)}|k><k|H^{(1)}|i>}{(\epsilon_i^{(0)} - \epsilon_k^{(0)})^2}
$$

Therefore

$$
\boxed{\epsilon_i^{(3)} = \sum_{kj\neq i} \frac{<i|H^{(1)}|j><j|H^{(1)}|k><k|H^{(1)}|i>}{(\epsilon_i^{(0)} - \epsilon_j^{(0)})(\epsilon_i^{(0)} - \epsilon_k^{(0)})} - \epsilon_i^{(1)} \sum_{k\neq i} \frac{<i|H^{(1)}|k><k|H^{(1)}|i>}{(\epsilon_i^{(0)} - \epsilon_k^{(0)})^2}} \tag{17.19}
$$

Alternatively, $\epsilon_i^{(1)} = <i|H^{(1)}|i>$ so that

$$
\boxed{\epsilon_i^{(3)} = \sum_{kj\neq i} \frac{<i|H^{(1)}|j><j|H^{(1)}|k><k|H^{(1)}|i>}{(\epsilon_i^{(0)} - \epsilon_j^{(0)})(\epsilon_i^{(0)} - \epsilon_k^{(0)})} - <i|H^{(1)}|i> \sum_{k\neq i} \frac{<i|H^{(1)}|k><k|H^{(1)}|i>}{(\epsilon_i^{(0)} - \epsilon_k^{(0)})}} \tag{17.20}
$$

Chapter 18

Degenerate perturbation theory

The perturbation theory presented earlier was called non-degenerate perturbation theory and only applied to states that were non-degenerate. However, in many cases one encounters degenerate states and an external perturbation acts to remove this intrinsic degeneracy. An example is the case of a particle in a symmetric 3D box where some external force elongates one of the sides of the box.

Previously you saw that the non-degenerate energy corrections as well as coefficients for the corected wavefunctions depended, inversely on the zero-order energy differences between the basis states.

$$\begin{aligned}\epsilon^{(2)} &= \sum_k \frac{<k|H^{(1)}|i><i|H^{(1)}|k>}{(\epsilon_i^{(0)} - \epsilon_k^{(0)})} = \frac{|<k|H^{(1)}|i>|^2}{(\epsilon_i^{(0)} - \epsilon_k^{(0)})} \\ |\Psi>_{tot} &= |i> + \sum_k \frac{<k|H^{(1)}|i>}{(\epsilon_i^{(0)} - \epsilon_k^{(0)})}|k>\end{aligned}$$

You can see that the expressions have a singularity if $\epsilon_i^{(0)} = \epsilon_k^{(0)}$

This problem arises because there is a fundamental ambiguity in the choice of zero order wavefunctions because any linear combination of these zero order wavefunctions is an eigenfunction of the Hamiltonian with the same energy.

To demonstrate, let's take a state with principal quantum number n. Let's use another letter to denote the degenerate state. For example, assume two degenerate states l and m.

$$|n, l>$$
$$|n, m>$$

Degenerate states of the Hamiltonian H. We then have

$$\begin{aligned} H|n, l> &= \epsilon|n, l> \\ H|n, m> &= \epsilon|n, m> \end{aligned}$$

Now suppose we take some linear combination of $|n, l>$ and $|n, m>$ say

$$|\Psi> = a|n, l> + b|n, m>$$

where a and b are some constants

$$\begin{aligned} H|\Psi> &= H[a|n, l> + b|n, m>] \\ &= aH|n, l> + bH|n, m> \\ &= a\epsilon|n, l> + b\epsilon|n, m> \\ &= \epsilon(a|n, l> + b|n, m>) \\ &= \epsilon|\Psi> \end{aligned}$$

Therefore

$$H|\Psi>= \epsilon|\Psi>$$

This shows that the zero order wavefunctions of a degenerate system are not well defined. Any linear combinations of degenerate states is itself an eigenfunction of the Hamiltonian H.

The first step in degenerate perturbation theory is therefore to find the correct linear combination of degenerate states to make a well defined zero order wavefunction. In matrix-speak you have to diagonalize the degenerate subspace.

To this end, the correct linear combination of degenerate zero-order functions are obtained by solving a set of secular equations and more specifically by solving a secular determinant.

This is abstract. Consider the zero-order energy level, n, with degeneracy g_n and energy $\epsilon_n^{(0)}$. Suppose that the correct choice for the zero order wavefunction is the linear combination

$$\Psi^{(0)} = \sum_j^g c_j|n, j>$$

where $|n, j>$ are the complete set of individual zero order wavefunctions that span the degenerate space.

From our previous expression derived from shoving

$$\begin{aligned}
\Psi_i &= \Psi_i^{(0)} + \lambda\Psi_i^{(1)} + \lambda^2\Psi_i^{(2)} + \ldots \\
\epsilon_i &= \epsilon_i^{(0)} + \lambda\epsilon_i^{(1)} + \lambda^2\epsilon_i^{(2)} + \ldots \\
H &= H^{(0)} + \lambda H^{(1)} + \lambda^2 H^{(2)} + \ldots \qquad (18.1)
\end{aligned}$$

into the Schrodinger equation $H\Psi = \epsilon\Psi$ we got a series of expressions with different orders of λ. Just focus on the 1st order expression which was

$$\boxed{(H^{(0)} - \epsilon_i^{(0)})\Psi_i^{(1)} + (H^{(1)} - \epsilon_i^{(1)})\Psi_i^{(0)} = 0}$$

we shove in our $\Psi^{(0)} = \sum_j^g c_j|n, j>$ to get

$$(H^{(0)} - \epsilon_n^{(0)})\Psi_i^{(1)} + (H^{(1)} - \epsilon_n^{(1)})\sum_j^g c_j|n, j>= 0$$

Now multiply both sides/integrate with $< n, k|$ to get

$$< n, k|H^{(0)} - \epsilon_i^{(0)}|\Psi_i^{(1)} > + \sum_j^g c_j < n, k|H^{(1)} - \epsilon_n^{(1)}|n, j >= 0$$

Here $H^{(0)}$ acting on $< n, k|$ gives $\epsilon_k^{(0)}$ but since $\epsilon_k^{(0)} = \epsilon_i^{(0)}$ due to them being degenerate, they cancel.

$$\boxed{\sum_j^g c_j < n, k|H^{(1)} - \epsilon_n^{(1)}|n, j >= 0} \qquad (18.2)$$

There are g many of these equations, one for every degenerate level j and each equations is a sum of g values as we run through all possible values of k.

We get

$$\begin{aligned}
c_1 < 1|H^{(1)} - \epsilon_n^{(1)}|1 > +c_2 < 1|H^{(1)} - \epsilon_n^{(1)}|2 > + \ldots c_g < \ |H^{(1)} - \epsilon_n^{(1)}|\ > &= 0 \\
c_1 < 2|H^{(1)} - \epsilon_n^{(1)}|1 > +c_2 < 2|H^{(1)} - \epsilon_n^{(1)}|2 > + \ldots c_g < \ |H^{(1)} - \epsilon_n^{(1)}|\ > &= 0 \\
c_1 < 3|H^{(1)} - \epsilon_n^{(1)}|1 > +c_2 < 3|H^{(1)} - \epsilon_n^{(1)}|2 > + \ldots c_g < \ |H^{(1)} - \epsilon_n^{(1)}|\ > &= 0 \\
c_1 < 4|H^{(1)} - \epsilon_n^{(1)}|1 > +c_2 < 4|H^{(1)} - \epsilon_n^{(1)}|2 > + \ldots c_g < \ |H^{(1)} - \epsilon_n^{(1)}|\ > &= 0 \\
\text{etc...}
\end{aligned}$$

or

$$\begin{pmatrix} <1|H^{(1)}-\epsilon_n^{(1)}|1> & <1|H^{(1)}-\epsilon_n^{(1)}|2> & \dots \\ <2|H^{(1)}-\epsilon_n^{(1)}|1> & <2|H^{(1)}-\epsilon_n^{(1)}|2> & \dots \\ <3|H^{(1)}-\epsilon_n^{(1)}|1> & <3|H^{(1)}-\epsilon_n^{(1)}|2> & \dots \\ <4|H^{(1)}-\epsilon_n^{(1)}|1> & <4|H^{(1)}-\epsilon_n^{(1)}|2> & \dots \\ \dots & \dots & \dots \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \\ \dots \end{pmatrix} = 0$$

This is called a set of secular equations. In matrix form it can be written as

$$(H^{(1)} - \epsilon_n^{(1)} I)c = 0$$

where I is the identity matrix and $H^{(1)}$ is the $g \times g$ matrix and c is a $g \times 1$ vector and 0 is a $g \times 1$ vector of all zeros.

Now the solution to this is found by solving the secular determinant.

$$|H^{(1)} - \epsilon_n^{(1)} I| = 0$$

When you do this you will find the correct values of c_j that in turn will give you the correct zero order wavefunctions.

In addition, the first order energy corrections with the perturbation present, $\epsilon^{(1)}$ are the eigenvalues of the $H^{(1)}$ matrix.

Don't forget that you are only dealing with the degenerate subspace. There could be other states that are also involved in the perturbation. However, you can include these corrections to the energies and wavefunctions using non-degenerate perturbation theory (now that you lifted the degeneracy).

Zeeman effect, doubly degenerate state

Consider an electron state in the xy plane which is doubly degenerate. Now apply a magnetic field along the z direction (Zeeman effect). The perturbation Hamiltonian is

$$\boxed{H^{(1)} = g\mu_B B\hat{l}_z} \tag{18.3}$$

where g is the g-value (2.0023), μ_B is the Bohr magneton, B is the magnetic field and $\hat{l}_z$ is the z component of the angular momentum operator $\hat{l}_z = -i\hbar\frac{\partial}{\partial\phi}$.

Let's say my two degenerate wavefunctions are

$$\begin{aligned}|a> &= \frac{1}{\sqrt{\pi}}sinm\phi\\ |b> &= \frac{1}{\sqrt{\pi}}cosm\phi\end{aligned}$$

where m is an integer.

Construct the secular determinant.

$$\begin{aligned}H|a> &= \frac{1}{\sqrt{\pi}}g\mu_B B(-i\hbar)\frac{\partial}{\partial\phi}(sinm\phi)\\ &= -\frac{i\hbar g\mu_B B}{\sqrt{\pi}}(m)cosm\phi\\ &= -\frac{i\hbar g\mu_B mB}{\sqrt{\pi}}cosm\phi\end{aligned}$$

$$\boxed{H|a>= -i\hbar g\mu_B mB|b>}$$

Next

$$\begin{aligned}H|b> &= i\hbar g\mu_B B\frac{m}{\sqrt{\pi}}sinm\phi\\ &= i\hbar g\mu_B mB|a>\end{aligned}$$

$$\boxed{H|b>= i\hbar g\mu_B mB|a>} \tag{18.4}$$

So the 2x2 that we construct is

$$\begin{pmatrix}<a|\hat{H}|a> & <a|\hat{H}|b>\\ <b|\hat{H}|a> & <b|\hat{H}|b>\end{pmatrix}$$

where

$$\begin{aligned}<a|\hat{H}|a> &= \frac{1}{\sqrt{\pi}}sinm\phi(-i\hbar g\mu_B mB)\frac{1}{\sqrt{\pi}}cosm\phi\\ &= A\int_0^{2n\pi} sinm\phi cosm\phi d\phi\\ &= \frac{A}{2}\int_0^{2n\pi} sin2m\phi d\phi\\ &= -\frac{A}{2}\frac{1}{2m}cos2m\phi|_0^{2n\pi} = 0\end{aligned}$$

and

$$\begin{aligned}
< b|\hat{H}|b > &= \frac{1}{\sqrt{\pi}} cosm\phi(i\hbar g\mu_B mB)\frac{1}{\sqrt{\pi}} sinm\phi \\
&= A\int_0^{2n\pi} sinm\phi cosm\phi d\phi = 0
\end{aligned}$$

and

$$\begin{aligned}
< a|\hat{H}|b > &= (\frac{1}{\sqrt{\pi}} sinm\phi)(i\hbar g\mu_B mB)(\frac{1}{\sqrt{\pi}} sinm\phi) \\
&= A\int_0^{2n\pi} sin^2 m\phi d\phi \\
&= \frac{A}{2}\int_0^{2n\pi} 1 - cos2m\phi d\phi \\
&= \frac{A}{2}\left[2n\pi - \int_0^{2n\pi} cos2m\phi d\phi\right] \\
&= An\pi - \frac{A}{2}\left(\frac{1}{2m}\right) sin2m\phi|_0^{2n\pi} \\
&= An\pi
\end{aligned}$$

where $A = \frac{1}{\pi}(i\hbar g\mu_B mB)$. Finally

$$\begin{aligned}
< b|\hat{H}|a > &= (\frac{1}{\sqrt{\pi}} cosm\phi)(-i\hbar g\mu_B mB)(\frac{1}{\sqrt{\pi}} cosm\phi) \\
&= -A\int_0^{2n\pi} cos^2 m\phi d\phi \\
&= -\frac{A}{2}\int_0^{2n\pi} 1 + cos2m\phi d\phi \\
&= -\frac{A}{2}\left[2n\pi + \int_0^{2n\pi} cos2m\phi d\phi\right] \\
&= -An\pi - \frac{A}{2}\left(\frac{1}{2m}\right) sin2m\phi|_0^{2n\pi} \\
&= -An\pi
\end{aligned}$$

where $A = \frac{1}{\pi}(i\hbar g\mu_B mB)$

Summary

$$\boxed{< a|\hat{H}|a >= 0} \tag{18.5}$$

$$\boxed{< a|\hat{H}|b >= i\hbar g\mu_B mB} \tag{18.6}$$

$$\boxed{< b|\hat{H}|a >= -i\hbar g\mu_B mB} \tag{18.7}$$

$$\boxed{< b|\hat{H}|b >= 0} \tag{18.8}$$

The secular equations are

$$\begin{pmatrix} 0-\epsilon^{(1)} & i\hbar g\mu_B mB \\ -i\hbar g\mu_B mB & 0-\epsilon^{(1)} \end{pmatrix} \begin{pmatrix} c_a \\ c_b \end{pmatrix} = 0$$

leading to the secular determinant (since we don't want the trivial solution, $c_a = c_b = 0$)

$$\begin{vmatrix} -\epsilon^{(1)} & i\hbar g\mu_B mB \\ -i\hbar g\mu_B mB & -\epsilon^{(1)} \end{vmatrix} = 0$$

which evaluates as

$$\begin{aligned} \epsilon^{(1)^2} - [\hbar^2 g^2 \mu_B^2 m^2 B^2] &= 0 \\ \epsilon^{(1)^2} &= (\hbar g\mu_B mB)^2 \end{aligned}$$

or

$$\boxed{\epsilon^{(1)} - \pm\hbar g\mu_B mB} \tag{18.9}$$

Now that we have our 1st order energy corrections we go and find the coefficients c_a and c_b to get he correct lienar combination for the zero order wavefunctions.

First for $\epsilon^{(1)}$ using (+) solution

$$\begin{pmatrix} -\hbar g\mu_B mB & i\hbar g\mu_B mB \\ -i\hbar g\mu_B mB & -\hbar g\mu_B mB \end{pmatrix} \begin{pmatrix} c_a \\ c_b \end{pmatrix} = 0$$

for simplicity let $a = \hbar g\mu_B mB$ to get

$$\begin{pmatrix} -a & ia \\ -ia & -a \end{pmatrix} \begin{pmatrix} c_a \\ c_b \end{pmatrix} = 0$$

Solve this however you want, Gauss-Jordan elimination etc...

$$-i * 1 \rightarrow 1$$

$$\begin{pmatrix} ia & a \\ -ia & -a \end{pmatrix} \begin{pmatrix} c_a \\ c_b \end{pmatrix} = 0$$

$$1 + 2 \rightarrow 2$$

$$\begin{pmatrix} ia & a \\ 0 & 0 \end{pmatrix} \begin{pmatrix} c_a \\ c_b \end{pmatrix} = 0$$

Therefore c_b can be anything. From the first equation we get $c_a = ic_b$ such that our desired eigenvector is

$$\boxed{c_b \begin{pmatrix} i \\ 1 \end{pmatrix}} \tag{18.10}$$

Next for $\epsilon^{(1)}$ using (-) solution

$$\begin{pmatrix} \hbar g\mu_B mB & i\hbar g\mu_B mB \\ -i\hbar g\mu_B mB & \hbar g\mu_B mB \end{pmatrix} \begin{pmatrix} c_a \\ c_b \end{pmatrix} = 0$$

let $a = \hbar g\mu_B mB$ for convenience giving

$$\begin{pmatrix} a & ia \\ -ia & a \end{pmatrix} \begin{pmatrix} c_a \\ c_b \end{pmatrix} = 0$$

$$i1 \rightarrow 1$$

$$\begin{pmatrix} ia & -a \\ -ia & a \end{pmatrix} \begin{pmatrix} c_a \\ c_b \end{pmatrix} = 0$$

$$1 + 2 \rightarrow 2$$

$$\begin{pmatrix} ia & -a \\ 0 & 0 \end{pmatrix} \begin{pmatrix} c_a \\ c_b \end{pmatrix} = 0$$

It is apparent that c_b can be anything. We evaluate $c_a = -ic_b$ giving our desired eigenvector

$$\boxed{c_b \begin{pmatrix} -i \\ 1 \end{pmatrix}} \tag{18.11}$$

Summary

$$\boxed{\Psi_+ = \frac{1}{\sqrt{2}}(i|a> + |b>)} \tag{18.12}$$

$$\boxed{\Psi_- = \frac{1}{\sqrt{2}}(-i|a> + |b>)} \tag{18.13}$$

These are the correct linear combinations of zero order wavefunctions.

The first order energy corrections are

$$\boxed{\epsilon_+^{(1)} = \hbar g \mu_B m B} \tag{18.14}$$

$$\boxed{\epsilon_-^{(1)} = -\hbar g \mu_B m B} \tag{18.15}$$

Examples

Example 1

An example using nondegenerate perturbation theory to get warmed up. We will do this to second order in the energies.

$$H = \begin{pmatrix} 0 + 0.5\lambda & 0.8\lambda & 0.4\lambda \\ 0.8\lambda & 2 + 0.4\lambda & 0.6\lambda \\ 0.4\lambda & 0.6\lambda & 4 - 0.2\lambda \end{pmatrix}$$

You can see here that the diagonal elements are non-degenerate. Specifically, the perturbations to these energies are smaller that half the splitting between states. This confirms that non-degenerate perturbation theory is appropriate.

With regard to the energies, you can already begin to read them off. The zeroth order energies are

$$\boxed{\epsilon_0^{(0)} = 0} \tag{18.16}$$

$$\boxed{\epsilon_1^{(0)} = 2} \tag{18.17}$$

$$\boxed{\epsilon_2^{(0)} = 4} \tag{18.18}$$

The 1st order corrections to these energies are

$$\boxed{\epsilon_0^{(1)} = 0.5} \tag{18.19}$$

$$\boxed{\epsilon_1^{(1)} = 0.4} \tag{18.20}$$

$$\boxed{\epsilon_2^{(1)} = -0.2} \tag{18.21}$$

Using our previous results from non-degenerate perturbation theory we get

$$\begin{aligned}\epsilon_0^{(2)} &= \frac{(0.8)^2}{(0-2)} + \frac{(0.4)^2}{(0-4)} \\ &= -\frac{0.64}{2} - \frac{0.16}{4} \\ &= -0.32 - 0.04 \\ &= -0.36\end{aligned}$$

Our second order correction to the base energy of state 0 is

$$\boxed{\epsilon_0^{(2)} = -0.36} \tag{18.22}$$

Next

$$\begin{aligned}\epsilon_1^{(2)} &= \frac{(0.8)^2}{(2-0)} + \frac{(0.6)^2}{(2-4)} \\ &= \frac{0.64}{2} - \frac{0.36}{2} \\ &= \frac{0.28}{2} \\ &= 0.14\end{aligned}$$

Our second order correction to the base energy of state 1 is

$$\boxed{\epsilon_1^{(2)} = 0.14} \tag{18.23}$$

Next

$$\begin{aligned}\epsilon_2^{(2)} &= \frac{(0.4)^2}{(4-0)} + \frac{(0.6)^2}{(4-2)} \\ &= \frac{0.16}{4} + \frac{0.36}{2} \\ &= 0.04 + 0.18 \\ &= 0.22\end{aligned}$$

Our desired second order correction to the base energy of state 2 is

$$\boxed{\epsilon_2^{(2)} = 0.22} \tag{18.24}$$

Summary

$$\begin{aligned}
\epsilon_0 &= \epsilon_0^{(0)} + \epsilon_0^{(1)} + \epsilon_0^{(2)} = 0 + 0.5 - 0.36 = 0.14 \\
\epsilon_1 &= \epsilon_1^{(0)} + \epsilon_1^{(1)} + \epsilon_1^{(2)} = 2 + 0.4 + 0.14 = 2.18 \\
\epsilon_2 &= \epsilon_2^{(0)} + \epsilon_2^{(1)} + \epsilon_2^{(2)} = 4 - 0.2 + 0.22 = 4.02
\end{aligned}$$

Example 2

An example of almost degenerate states

$$H = \begin{pmatrix} 1+0.5\lambda & 0.8\lambda & 0.4\lambda \\ 0.8\lambda & 1+0.4\lambda & 0.6\lambda \\ 0.4\lambda & 0.6\lambda & 4-0.2\lambda \end{pmatrix}$$

Along the diagonal one can see two nearly degenerate states. So non-degenerate perturbation theory cannot be used for these two states although in principle it can be used for the third state at the bottom right. We know that the appropriate $|0>$ and $|1>$ states will be a linear combination of the zero order wavefunctions

$$\begin{aligned}
|0>^{'} &= a|0> + b|1> \\
|1>^{'} &= c|0> + d|1>
\end{aligned}$$

Now you can go ahead and brute force it by solving the full secular etermi-nant exactly or you can take the degenerate perturbation theory approach and only diagonalize the degenerate subblock. So do either

$$\begin{vmatrix} 1+0.5\lambda-\epsilon & 0.8\lambda & 0.4\lambda \\ 0.8\lambda & 1+0.4\lambda-\epsilon & 0.6\lambda \\ 0.4\lambda & 0.6\lambda & 4-0.2\lambda-\epsilon \end{vmatrix} = 0$$

or

$$\begin{vmatrix} 1+0.5\lambda-\epsilon & 0.8\lambda \\ 0.8\lambda & 1+0.4\lambda-\epsilon \end{vmatrix} = 0$$

or better yet just leave out the zero order base energies and solve

$$\begin{vmatrix} 0.5\lambda - \epsilon^{(1)} & 0.8\lambda \\ 0.8\lambda & 0.4\lambda - \epsilon^{(1)} \end{vmatrix} = 0$$

Let's solve the third determinant.

$$\begin{aligned} (0.5 - \epsilon^{(1)})(0.4 - \epsilon^{(1)}) - 0.64 &= 0 \\ 0.2 - 0.5\epsilon^{(1)} - 0.4\epsilon^{(1)} + \epsilon^{(1)^2} - 0.64 &= 0 \\ \epsilon^{(1)^2} - 0.9\epsilon^{(1)} - 0.44 &= 0 \end{aligned}$$

We know the solutions to the quadratic equation to get

$$\begin{aligned} \epsilon^{(1)} &= \frac{0.9 \pm \sqrt{0.81 + 4(1)(0.44)}}{2} \\ &= \frac{0.9 \pm \sqrt{0.81 + 1.76}}{2} \\ &= \frac{0.9 \pm \sqrt{2.57}}{2} \\ &= \frac{0.9 \pm 1.603}{2} \end{aligned}$$

We therefore have

$$\epsilon^{(1)} = \frac{0.9 + 1.6}{2} = \frac{2.5}{2} = 1.25\lambda$$
$$\epsilon^{(1)} = \frac{0.9 - 1.6}{2} = \frac{0.7}{2} = -0.35\lambda$$

These are our first order energy corrections to lift the degeneracy in the presence of our perturbation. The corrected energies are

$$\boxed{\epsilon_0 = 1 - 0.35\lambda} \tag{18.25}$$

$$\boxed{\epsilon_1 = 1 + 1.25\lambda} \tag{18.26}$$

Recall from before that now you know $\epsilon^{(1)}$ you can go after the correct coefficients (a,b,c,d) where $|0>= a|0> +b|1>$ and $|1>= c|0> +d|1>$. And since ϵ_2 was non-degenerate to begin with we could have used non-degenerate perturbation theory to get ϵ_2 corrected from the start if we only wanted ϵ_2.

$$\begin{aligned}\epsilon_2 &= 4 - 0.2\lambda + \frac{(0.4\lambda)^2}{(4-1)} + \frac{(0.1\lambda)^2}{(4-1)} \\ &= 4 - 0.2\lambda + \frac{0.16\lambda^2}{3} + \frac{0.36\lambda^2}{3} \\ &= 4 - 0.2\lambda + \frac{0.50\lambda^2}{3}\end{aligned}$$

giving

$$\boxed{\epsilon_2 = 4 - 0.2\lambda + 0.17\lambda^2} \tag{18.27}$$

Corrected to second order using non-degenerate perturbation theory.

However, in practice if you diagonalize a degenerate subblock (leading to $|0>'$ and $|1>'$ as linear combinations of original zero order wavefunctions)

$$\begin{aligned}|0>' &= a|0> + b|1> \\ |1>' &= c|0> + d|1>\end{aligned}$$

you should probably recalculate all other off diagonal elements.

So let's take our previous example and make it truly degenerate for the purpose of this example.

$$H = \begin{pmatrix} 1+0.5\lambda & 0.8\lambda & 0.4\lambda \\ 0.8\lambda & 1+0.5\lambda & 0.6\lambda \\ 0.4\lambda & 0.6\lambda & 4-0.2\lambda \end{pmatrix} \tag{18.28}$$

We diagonalize the degenerate subblock. You can do this by solving for either ϵ or for $\epsilon^{(1)}$. Just remember what you are solving for. Here we do it for ϵ.

$$\begin{vmatrix} 1.5-\epsilon & 0.8 \\ 0.8 & 1.5-\epsilon \end{vmatrix} = 0$$

giving

$$\begin{aligned}(1.5-\epsilon)^2 - 0.8^2 &= 0 \\ (1.5-\epsilon)^2 &= 0.8^2 \\ 1.5\epsilon &= \pm 0.8 \\ \epsilon &= 1.5 \pm 0.8\end{aligned}$$

yielding

$$\boxed{\epsilon_0 = 0.7} \tag{18.29}$$

$$\boxed{\epsilon_1 = 2.3} \tag{18.30}$$

These are our new energies for states 0 and 1. Putting these back into the original matrix we get

$$H = \begin{pmatrix} 0.7 & 0 & 0.4^* \\ 0 & 2.3 & 0.6^* \\ 0.4^* & 0.6^* & 4-0.2 \end{pmatrix}$$

Now we go after the terms with asterisks. First though we should find our eigenvectors

Case 1, $\epsilon_0 = 0.7$

$$\begin{pmatrix} 1.5-0.7 & 0.8 \\ 0.8 & 1.5-0.7 \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix} = 0$$

$$\begin{pmatrix} 0.8 & 0.8 \\ 0.8 & 0.8 \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix} = 0$$

$$-1 + 2 \rightarrow 2$$

$$\begin{pmatrix} 0.8 & 0.8 \\ 0 & 0 \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix} = 0$$

where b is anything and $a = -b$. We get

$$b \begin{pmatrix} -1 \\ 1 \end{pmatrix}$$

or let $b = -1$ for convenience

$$= \begin{pmatrix} 1 \\ -1 \end{pmatrix}$$

The normalization constant of this vector is $\frac{1}{\sqrt{2}}$. Put it all together and get

$$\boxed{|0>' = \frac{1}{\sqrt{2}}(|0> - |1>)} \tag{18.31}$$

Case 2, $\epsilon_0 = 2.3$

$$\begin{pmatrix} 1.5-2.3 & 0.8 \\ 0.8 & 1.5-2.3 \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix} = 0$$

$$\begin{pmatrix} -0.8 & 0.8 \\ 0.8 & -0.8 \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix} = 0$$

$$1 + 2 \rightarrow 2$$

$$\begin{pmatrix} -0.8 & 0.8 \\ 0 & 0 \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix} = 0$$

So b can be anything. Let $b = 1$

$$\begin{aligned} &= b\begin{pmatrix} 1 \\ 1 \end{pmatrix} \\ &= \begin{pmatrix} 1 \\ 1 \end{pmatrix} \end{aligned} \tag{18.32}$$

The normaliztion constant is $\frac{1}{\sqrt{2}}$. Now putting it all together the wavefunction is

$$\boxed{|1>^{'} = \frac{1}{\sqrt{2}}(|0> + |1>)} \tag{18.33}$$

Now we can go and re-evaluate all our off diagonal elements when dealing with $|2>$.

$$\begin{aligned} <0^{'}|H^{(1)}|2> &= \frac{1}{\sqrt{2}}(<0| - <1|)H^{(1)}|2> \\ &= \frac{1}{\sqrt{2}}[<0|H^{(1)}|2> - <1|H^{(1)}|2>] \\ &= \frac{1}{\sqrt{2}}[0.4 - 0.1] \\ &= \frac{1}{\sqrt{2}}(-0.2) \\ &= -0.1414 \end{aligned}$$

$$\boxed{<0^{'}|H^{(1)}|2> = -0.1414} \tag{18.34}$$

Next

$$\begin{aligned}
< 1'|H^{(1)}|2 > &= \frac{1}{\sqrt{2}}(< 0| + < 1|)H^{(1)}|2 > \\
&= \frac{1}{\sqrt{2}}[< 0|H^{(1)}|2 > + < 1|H^{(1)}|2 >] \\
&= \frac{1}{\sqrt{2}}[0.4 + 0.6] \\
&= \frac{1}{\sqrt{2}}(1) \\
&= 0.7071
\end{aligned}$$

$$\boxed{< 1'|H^{(1)}|2 >= 0.7071} \tag{18.35}$$

Now put everything back together

$$\boxed{H = \begin{pmatrix} 0.7 & 0 & -0.1414 \\ 0 & 2.3 & 0.7071 \\ -0.1414 & 0.7071 & 4 - 0.2 \end{pmatrix}} \tag{18.36}$$

Now can do ϵ_2 up to second order in non-degenerate perturbation theory.

2nd order degenerate perturbation theory

But sometimes 1st order degenerate perturbation theory may not totally lift all the degeneracies, especially if the perturbation $H^{(1)}$ does not couple the degenerate levels. For example

$$H = \begin{pmatrix} 1 + 0.1\lambda & 0 & 0.4\lambda \\ 0 & 1 + 0.1\lambda & 0.6\lambda \\ 0.4\lambda & 0.6\lambda & 4 - 0.2\lambda \end{pmatrix}$$

The top left corner of the matrix reveals the degenerate subblock where you can see that no off diagonals connect the two degenerate states.

We also cannot use 2nd order non-degenerate perturbation theory. Are we stuck? No, we can use 2nd order degenerate perturbation theory.

Formally, you assume that

- $H_{jk} = 0$, (no off diagonals coupling the levels and where j,k are $(j \neq k)$ degenerate levels)

- $H_{jj}^{(1)} = \epsilon_m^{(1)}$
- Like before, assume that the wavefunction has the form: $|m >= \sum_{k=1}^{g} c_k |k^{(0)} > +\lambda |m^{(1)} > +\lambda^2 |m^{(2)} > + \ldots$ where g is the degeneracy of the level and the sum is to express the "true" zero order wavefunction as a linear combination of the degenerate original zero order wavefunctions
- Next assume $H = H^{(0)} + \lambda H^{(1)}$ where there are no second order terms in the Hamiltonian. Only consider things to 1st order here.
- Also $\epsilon = \epsilon^{(0)} + \lambda \epsilon_m^{(1)} + \lambda^2 \epsilon_m^{(2)} + \ldots$

Now plug everything into the Schrodinger equation.

$$\begin{aligned} H\Psi &= \epsilon\Psi \\ & (H^{(0)} + \lambda H^{(1)})[\sum_{k=1}^{g} c_k |k^{(0)} > +\lambda |m^{(1)} > +\lambda^2 |m^{(2)} >] \\ &= (\epsilon^{(0)} + \lambda \epsilon_m^{(1)} + \lambda^2 \epsilon_m^{(2)})[\sum_{k=1}^{g} c_k |k^{(0)} > +\lambda |m^{(1)} > +\lambda^2 |m^{(2)} >] \end{aligned}$$

We expand this expression and equate the powers of λ like we did in the non-degenerate section. (This derivation will be slightly different though)

For λ^0

$$H^{(0)} \sum_{k=1}^{g} c_k |k^{(0)} >= \epsilon^{(0)} \sum_{k=1}^{g} c_k |k^{(0)} >$$

$$\boxed{(H^{(0)} - \epsilon^{(0)}) \sum_{k=1}^{g} c_k |k^{(0)} >} \tag{18.37}$$

For λ^1

$$\lambda H^{(0)} |m^{(1)} > +\lambda H^{(1)} \sum_{k=1}^{g} c_k |k^{(0)} >= \lambda \epsilon^{(0)} |m^{(1)} > +\lambda \epsilon_m^{(1)} \sum_{k=1}^{g} c_k |k^{(0)} >$$

$$\boxed{(H^{(1)} - \epsilon_m^{(1)}) \sum_{k=1}^{g} c_k |k^{(0)} > +(H^{(0)} - \epsilon^{(0)}) |m^{(1)} >= 0} \tag{18.38}$$

For λ^2

$$\begin{aligned}\lambda^2 H^{(0)}|m^{(2)}> +\lambda^2 H^{(1)}|m^{(1)}> &= \lambda^2\epsilon^{(0)}|m^{(2)}> +\lambda^2\epsilon_m^{(1)}> +\lambda^2\epsilon_m^{(2)}\sum_{k=1}^{g} c_k|k^{(0)}> \\ (H^{(0)}-\epsilon_m^{(0)})|m^{(2)}> +(H^{(1)}-\epsilon_m^{(1)})|> &= \epsilon_m^{(2)}\sum_{k=1}^{g} c_k|k^{(0)}>\end{aligned}$$

$$\boxed{\epsilon_m^{(2)}\sum_{k=1}^{g} c_k|k^{(0)}>=(H^{(0)}-\epsilon_m^{(0)})|m^{(2)}> +(H^{(1)}-\epsilon_m^{(1)})|m^{(1)}>} \quad (18.39)$$

Now to derive an expression for the second order degenerate perturbation theory energies $\epsilon^{(2)}$ multiply/integrate the last expression by one of the degenerate zero order states $< j^{(0)}|$

$$\begin{aligned}\epsilon_m^{(2)}\sum_{k=1}^{g} c_k < j^{(0)}|k^{(0)}> &= < j^{(0)}|H^{(0)}-\epsilon_m^{(0)}|m^{(2)}> + < j^{(0)}|H^{(1)}-\epsilon_m^{(1)}|m^{(1)}> \\ & \quad j \text{ and } k \text{ are both from the degenerate space} \\ \epsilon_m^{(2)}c_{k=j}\delta_{kj} &= < j^{(0)}|H^{(1)}-\epsilon_m^{(1)}|m^{(1)}> \\ \epsilon_m^{(2)}c_{k=j}\delta_{kj} &= < j^{(0)}|H^{(1)}|m^{(1)}> -\epsilon_m^{(1)} < j^{(0)}|m^{(1)}>\end{aligned}$$

Now here we will insert the closure relation over all zero order states, both degenerate and non-degenerate. The closure relation recall is $\sum_n^{\infty}|n^{(0)}>< n^{(0)}|=1$. We then get

$$\epsilon_m^{(2)}c_{k=j}\delta_{kj}=\sum_n < j^{(0)}|H^{(1)}|n^{(0)}>< n^{(0)}|m^{(1)}> -\sum_n \epsilon_m^{(1)} < j^{(0)}|n^{(0)}>< n^{(0)}|m^{(1)}>$$

Now since n runs over both degenerate and non-degenerate states, split the sum into two. One part runs over all degenerate states and the other over all non-degenerate states $\sum=\sum_{n=ND}+\sum_{n=D}$ where ND=non-degenerate and D=degenerate.

$$\begin{aligned}\epsilon_m^{(2)}c_{k=j}\delta_{kj} &= \sum_{n=ND} < j^{(0)}|H^{(1)}|n^{(0)}>< n^{(0)}|m^{(1)}> \\ &- \epsilon_m^{(1)}\sum_{n=ND} < j^{(0)}|n^{(0)}>< n^{(0)}|m^{(1)}> \\ &+ \sum_{n=D} < j^{(0)}|H^{(1)}|n^{(0)}>< n^{(0)}|m^{(1)}> \\ &- \epsilon_m^{(1)}\sum_{n=D} < j^{(0)}|n^{(0)}>< n^{(0)}|m^{(1)}>\end{aligned}$$

Now look carefully. In the $\sum_{n=ND}$ part we have

$$-\epsilon_m^{(1)} \sum_{n=ND} < j^{(0)}|n^{(0)} >< n^{(0)}|m^{(1)} >$$

Here j belongs to the degenerate subspace whereas n by definition belongs to the ND subspace. Therefore this term=0. We are left with

$$\begin{aligned}
& \epsilon_m^{(2)} c_{k=j}\delta_{kj} \sum_{n=ND} < j^{(0)}|H^{(1)}|n^{(0)} >< n^{(0)}|m^{(1)} > \\
+ & \sum_{n=D} < j^{(0)}|H^{(1)}|n^{(0)} >< n^{(0)}|m^{(1)} > \\
- & \epsilon_m^{(1)} \sum_{n=ND} < j^{(0)}|n^{(0)} >< n^{(0)}|m^{(1)} > \\
= & \sum_{n=ND} < j^{(0)}|H^{(1)}|n^{(0)} >< n^{(0)}|m^{(1)} > \\
+ & \sum_{n=D} [< j^{(0)}|H^{(1)}|n^{(0)} > -\epsilon_m^{(1)}\delta_{jn}] < n^{(0)}|m^{(1)} >
\end{aligned}$$

Now here recall that j belongs to the degenerate subset as well as n. And that all off diagonal terms $= 0$ (this was one of our formal assumptions way at this beginning of this section.) We get

$$\begin{aligned}
\epsilon_m^{(2)} c_{k=j}\delta_{kj} \quad & \sum_{n=ND} < j^{(0)}|H^{(1)}|n^{(0)} >< n^{(0)}|m^{(1)} > \\
& + \sum_{n=D} [H_{j=n}^{(1)}\delta_{jn} - \epsilon_m^{(1)}\delta_{jn}] < n^{(0)}|m^{(1)} >
\end{aligned}$$

Now recall our second formal assumption that $H_{jj}^{(1)} = \epsilon_m^{(1)}$. This means that $\sum_{n=D}[H_{j=n}\delta_{jn} - \epsilon_m^{(1)}\delta_{jn}] < n^{(0)}|m^{(1)} >= 0$ leaving

$$\epsilon_m^{(2)} c_{k=j}\delta_{kj} = \sum_{n=ND} < j^{(0)}|H^{(1)}|n^{(0)} >< n^{(0)}|m^{(1)} >$$

Now the only catch is that we need to know what $< n^{(0)}|m^{(1)} >$ is. To do this go back to our 1st order expression

We have

$$(H^{(1)} - \epsilon_m^{(1)}) \sum_{k=1}^{g} c_k|k^{(0)} > +(H^{(0)} - \epsilon^{(0)})|m^{(1)} >= 0$$

and remember that k is part of our g degenerate subspace.

Now multiply/integrate by $< n^{(0)}|$ which is part of the non-degenerate subspace.

$$\begin{aligned} < n^{(0)}|H^{(1)} - \epsilon^{(1)}_m| \sum_{k=1}^{g} c_k |k^{(0)} > + < n^{(0)}|H^{(0)} - \epsilon^{(0)}|m^{(1)} > &= 0 \\ \sum_{k=1}^{g} < n^{(0)}|H^{(1)} - \epsilon^{(1)}_m|k^{(0)} > + < n^{(0)}|H^{(0)} - \epsilon^{(0)}|m^{(1)} > &= 0 \\ \sum_{k=1}^{g} c_k[< n^{(0)}|H^{(1)}|k^{(0)} > -\epsilon^{(1)}_m < n^{(0)}|k^{(0)} >] + < n^{(0)}|H^{(0)} - \epsilon^{(0)}_m|m^{(1)} > &= 0 \end{aligned}$$

Since n is part of the non-degenerate subspace and k is part of the degenerate subspace $< n^{(0)}|k^{(0)} >= 0$. We get

$$\sum_{k=1}^{g} c_k < n^{(0)}|H^{(1)}|k^{(0)} + < n^{(0)}|H^{(0)} - \epsilon^{(0)}|m^{(1)} >= 0$$

where $H^{(0)}|n^{(0)} >= \epsilon^{(0)}_n|n^{(0)} >$. So therefore $< n^{(0)}|H^{(0)} =< n^{(0)}|\epsilon^{(0)}_n$ (Hermitian).

$$\sum_{k=1}^{g} c_k < n^{(0)}|H^{(1)}|k^{(0)} > +(\epsilon^{(0)}_n - \epsilon^{(0)}) < n^{(0)}|m^{(1)} >= 0$$

Therefore

$$(\epsilon^{(0)} - \epsilon^{(0)}_n) < n^{(0)}|m^{(1)} >= \sum_{k=1}^{g} c_k < n^{(0)}|H^{(1)}|k^{(0)} >$$

giving our desired expression that will solve all things

$$\boxed{< n^{(0)}|m^{(1)} >= \sum_{k=1}^{g} c_k \frac{< n^{(0)}|H^{(1)}|k^{(0)} >}{(\epsilon^{(0)} - \epsilon^{(0)}_n)}} \tag{18.40}$$

Substitute this expression back into our original expression

$$\begin{aligned} \epsilon^{(2)}_m c_{k=j}\delta_{kj} &= \sum_{n=ND} < j^{(0)}|H^{(1)}|n^{(0)} >< n^{(0)}|m^{(1)} > \\ &= \sum_{n=ND} \sum_{k=1} \frac{< j^{(0)}|H^{(1)}|n^{(0)} >< n^{(0)}|H^{(1)}|k^{(0)} >}{(\epsilon^{(0)} - \epsilon^{(0)}_n)} c_k \end{aligned}$$

Consolidate everything

$$\begin{aligned}\sum_{n=ND}\sum_{k=1}^{g}\frac{< j^{(0)}|H^{(1)}|n^{(0)}>< n^{(0)}|H^{(1)}|k^{(0)}>}{(\epsilon^{(0)}-\epsilon_n^{(0)})}c_k-\epsilon_m^{(2)}c_{k=j}\delta_{kj} &= 0\\ \sum_{k=1}^{g}\left[\sum_{n=ND}\frac{< j^{(0)}|H^{(1)}|n^{(0)}>< n^{(0)}|H^{(1)}|k^{(0)}>}{(\epsilon^{(0)}-\epsilon_n^{(0)})}-\epsilon_m^{(2)}\delta_{kj}\right]c_k &= 0\end{aligned}$$

So if $c_k \neq 0$ then

$$\boxed{\sum_{k=1}^{g}\left[\sum_{n=ND}\frac{<j^{(0)}|H^{(1)}|n^{(0)}><n^{(0)}|H^{(1)}|k^{(0)}>}{(\epsilon^{(0)}-\epsilon_n^{(0)})}-\epsilon_m^{(2)}\delta_{kj}\right]=0} \qquad (18.41)$$

This is basically a series of equations which can be solved by doing the secular equation.

$$\boxed{\left|\sum_{n=ND}\frac{<j^{(0)}|H^{(1)}|n^{(0)}><n^{(0)}|H^{(1)}|k^{(0)}>}{(\epsilon^{(0)}-\epsilon_n^{(0)})}-\epsilon_m^{(2)}\delta_{kj}\right|=0} \qquad (18.42)$$

Another way to think of it is an eigenvalue problem where $\epsilon_m^{(2)}$ is our desired eigenvalue.

So you can see that the degenerate levels j and k couple to each other through the nondegenerate level n.

Example of 2nd order degenerate perturbation theory

$$H=\begin{pmatrix}1+0.1\lambda & 0 & 0.4\lambda\\ 0 & 1+0.1\lambda & 0.6\lambda\\ 0.4\lambda & 0.6\lambda & 4-0.2\lambda\end{pmatrix}$$

We need to solve

$$\left|\sum_{n=ND}\frac{H_{jn}H_{nk}}{\epsilon^{(0)}-\epsilon_n^{(0)}}-\epsilon_m^{(2)}\delta_{kj}\right|=0$$

So we already see that $n = 3$

$$
\begin{aligned}
\left| \sum_{n=3} \frac{H_{jn}H_{nk}}{\epsilon^{(0)} - \epsilon_n^{(0)}} - \epsilon_m^{(2)}\delta_{kj} \right| &= 0 \\
\begin{vmatrix} (j=1,k=1,n=3) & (j=1,k=2,n=3) \\ (j=2,k=1,n=3) & (j=2,k=2,n=3) \end{vmatrix} &= 0 \\
\begin{vmatrix} \frac{|H_{13}|^2}{1-4} - \epsilon_m^{(2)} & \frac{H_{13}H_{32}}{1-4} \\ \frac{H_{23}H_{31}}{1-4} & \frac{|H_{23}|^2}{1-4} - \epsilon_m^{(2)} \end{vmatrix} &= 0 \\
\begin{vmatrix} \frac{(0.4)^2}{-3} - \epsilon_m^{(2)} & \frac{(0.4)(0.6)}{-3} \\ \frac{(0.6)(0.4)}{-3} & \frac{(0.6)^2}{-3} - \epsilon_m^{(2)} \end{vmatrix} &= 0 \\
\begin{vmatrix} \frac{0.16}{-3} - \epsilon_m^{(2)} & \frac{0.24}{-3} \\ \frac{0.24}{-3} & \frac{0.36}{-3} - \epsilon_m^{(2)} \end{vmatrix} &= 0 \\
\begin{vmatrix} -0.0533 - \epsilon_m^{(2)} & -0.08 \\ -0.08 & -0.12 - \epsilon_m^{(2)} \end{vmatrix} &= 0
\end{aligned}
$$

giving

$$
\begin{aligned}
(0.0533 + \epsilon_m^{(2)})(0.12 + \epsilon_m^{(2)}) - (0.08)^2 &= 0 \\
0.0064 + 0.0533\epsilon_m^{(2)} + 0.12\epsilon_m^{(2)} + \epsilon_m^{(2)} - 0.0064 &= 0 \\
\epsilon_m^{(2)^2} + 0.1733\epsilon_m^{(2)} &= 0 \\
\epsilon_m^{(2)}(\epsilon_m^{(2)} + 0.1733) &= 0
\end{aligned}
$$

Our second order corrections are

$$\boxed{\epsilon_m^{(2)} = 0} \tag{18.43}$$

$$\boxed{\epsilon_m^{(2)} = -0.1733} \tag{18.44}$$

The total energies to second order in degenerate perturbation theory are then

$$\boxed{\epsilon_0 = 1 + 0.1 + 0 = 1.1} \tag{18.45}$$

$$\boxed{\epsilon_1 = 1 + 0.1 - 0.1733 = 0.9267} \tag{18.46}$$

If second order degenerate perturbation theory doesn't do the trick then

- you're in trouble
- and/or the levels will likely stay degenerate to all higher orders.

Chapter 19

The WKB Approximation

WKB stands for Wentzel, Kramers and Brillouin.

This is a technique for obtaining approximate solutions to the time-independent Schrodinger equation in 1D. It is very useful in calculating bound state energies and tunneling rates through potential barriers.

The method is a real life approach for tackling complicated potentials.

It works best with potentials that are almost constant relative to the wavelength of the particle.

Start with the Schrodinger equation and assume that the kinetic energy of the particle is greater than the potential ($\epsilon > V$).

$$-\frac{\hbar^2}{2m}\frac{d^2\Psi}{dx^2} + V(x)\Psi = \epsilon\Psi$$

Rewrite the equation as

$$\begin{aligned}
\frac{\hbar^2}{2m}\frac{d^2\Psi}{dx^2} &= (V-\epsilon)\Psi \\
\frac{d^2\Psi}{dx^2} &= \frac{2m(V-\epsilon)}{\hbar^2}\Psi \\
\frac{d^2\Psi}{dx^2} &= -\frac{2m(\epsilon-V)}{\hbar^2}\Psi \\
\frac{d^2\Psi}{dx^2} &= -k^2\Psi \\
\text{where } k^2 = \frac{2m(\epsilon-V)}{\hbar^2}
\end{aligned}$$

leaving

$$\boxed{\tfrac{d^2\Psi}{dx^2} + k^2\Psi = 0} \tag{19.1}$$

Now in general since the potential underneath the particle is slowly varying, both the amplitude and the phase of the wavefunction will change.

The general form of the wavefunction is

$$\Psi(x) = A(x)e^{i\phi(x)}$$

For shorthand just write this as $Ae^{i\phi}$.

Next we insert this form of the wavefunction into Schrodinger's equation above.

To begin, we evaluate some derivatives that we will need. The first derivative of the wavefunction is

$$\begin{aligned}\frac{d\Psi}{dx} &= Aie^{i\phi}\phi^{'} + A^{'}e^{i\phi} \\ &= (A^{'} + iA\phi^{'})e^{i\phi}\end{aligned}$$

Next we do the second derivative of the wavefunction

$$\begin{aligned}\frac{d^2\Psi}{dx^2} &= (A^{'} + iA\phi^{'})ie^{i\phi}\phi^{'} + e^{i\phi}[A^{''} + i(A\phi^{''} + A^{'}\phi^{'})] \\ &= (iA^{'}\phi^{'} - A\phi^{'2})e^{i\phi} + e^{i\phi}(A^{''} + iA\phi^{''} + iA^{'}\phi^{'}) \\ &= e^{i\phi}(iA^{'}\phi^{'} - A\phi^{'2} + A^{''} + iA\phi^{''} + iA^{'}\phi^{'}) \\ &= e^{i\phi}(2iA^{'}\phi^{'} - A\phi^{'2} + A^{''} + iA\phi^{''})\end{aligned}$$

Now we replace this expression into the above Schrodinger equation.

$$\begin{aligned}e^{i\phi}(2iA^{'}\phi^{'} - A\phi^{'2} + iA\phi^{''}) + k^2Ae^{i\phi} &= 0 \\ 2iA^{'}\phi^{'} - A\phi^{'2} + A^{''} + iA\phi^{''} + k^2A &= 0\end{aligned}$$

Group the real and imaginary terms. First let's do the real terms.

Real expression

$$-A\phi^{'2} + A^{''} + k^2A = 0$$

Imaginary expression

Next do the imaginary terms

$$\begin{aligned}2iA^{'}\phi^{'} + iA\phi^{''} &= 0 \\ 2A^{'}\phi^{'} + A\phi^{''} &= 0\end{aligned}$$

or

$$(A^2\phi^{'})^{'} = 0$$

Now we want to solve for A and ϕ so we can have an explicit form for our wavefunction. Solve the imaginary equation first.

$$\begin{aligned}(A^2\phi^{'})^{'} &= 0\\ A^2\phi^{'} &= C^2\\ \text{where } C^2 \text{ is a constant}\\ A^2 &= \frac{C^2}{\phi^{'}}\end{aligned}$$

giving

$$\boxed{A = \frac{C_\pm}{\sqrt{\phi^{'}}}} \tag{19.2}$$

where we have buried the sign in the constant $C_\pm$.

The real expression cannot be solved exactly. However, if A varies slowly, then $A^{''}$ is small and can be ignored. Hence the potential cannot be changing fast if this approximation is to work.

$$\begin{aligned}-A\phi^{'2} + k^2A &= 0\\ A\phi^{'2} &= k^2A\\ \phi^{'2} &= k^2\\ \phi^{'} &= \pm k\end{aligned}$$

We get

$$\boxed{\phi = \pm\int kdx} \tag{19.3}$$

In summary the total wavefunction is

$$\Psi = Ae^{i\phi}$$

or putting everything together we get

$$\boxed{\Psi = \frac{C_\pm}{\sqrt{k}}e^{\pm i\int kdx}} \tag{19.4}$$

where $k = \sqrt{\frac{2m(\epsilon - V)}{\hbar^2}}$ and where we also assumed that $(\epsilon > V)$

Example, Particle in a bumpy well

The potential of this problem looks like

- $V(x)$ is something say $F(x)$ for $0 < x < a$
- ∞ otherwise

Inside the well ($\epsilon > V$)

$$\begin{aligned}\Psi(x) &= \frac{1}{\sqrt{k}}(C_+ e^{i\phi} + C_- e^{-i\phi}) \\ &\quad \text{where recall that } \phi = \int k dx \\ &\simeq \frac{1}{\sqrt{k}}(C_1 cos\phi + C_2 sin\phi)\end{aligned}$$

where

- $\Psi(0) = 0 \rightarrow \phi = 0$ or $C_1 = 0$
- $\Psi(a) = 0 \rightarrow sin\phi = 0$ or $\phi = n\pi$

giving

$$\simeq \frac{1}{\sqrt{k}}(C_2 sin\phi)$$

or

$$\boxed{\int_0^a k dx = n\pi} \tag{19.5}$$

where $n = 1, 2, 3, \ldots$ or

$$\boxed{\int_0^a \sqrt{\frac{2m(\epsilon - V(x))}{\hbar^2}} dx = n\pi} \tag{19.6}$$

So this restricts the possible values of ϵ. Note however that if $V(x) = 0$ we can reduce this expression to something that looks pretty familiar.

$$\begin{aligned}
\int_0^a \sqrt{\frac{2m\epsilon}{\hbar^2}} dx &= n\pi \\
\sqrt{\frac{2m\epsilon}{\hbar^2}} a &= n\pi \\
\sqrt{\frac{2m\epsilon}{\hbar^2}} &= \frac{n\pi}{a} \\
\frac{2m\epsilon}{\hbar^2} &= \frac{n^2\pi^2}{a^2} \\
\epsilon &= \frac{n^2\pi^2\hbar^2}{2ma^2} \\
\epsilon &= \frac{n^2h^2}{8ma^2}
\end{aligned}$$

The energies of the particle in the bumpy box are

$$\boxed{\epsilon = \frac{n^2h^2}{8ma^2}} \qquad (19.7)$$

We get back the standard particle in a box energies.

Chapter 20

Time dependent perturbation theory

So how do you treat time dependent phenomena? That is where the Hamiltonian is time dependent.

For example, one of the most prominent examples is the interaction of a molecule or atom with light. Or the collision of two molecules. Or the collision of an electron and a molecule etc...

This is where we invoke another kind of perturbation theory called- time dependent perturbation theory. (as opposed to time independent perturbation theory which we did earlier.)

To begin with, let's re-derive the expression of the general wavefunctions of stationary states. The general form of Schrodinger's equation is

$$\begin{aligned} i\hbar\frac{\partial}{\partial t}\Psi(r,t) &= H\Psi(r,t) \\ &\quad \text{where } H = -\frac{\hbar^2\nabla^2}{2m} + V \\ i\hbar\frac{\partial}{\partial t}\Psi(r,t) &= \left(-\frac{\hbar^2\nabla^2}{2m} + V\right)\Psi(r,t) \end{aligned}$$

In the case of a time independent perturbation we have $V = V(r)$.

Look for solutions of the form

$$\Psi(r,t) = \Psi(r)f(t)$$

For shorthand reduce this to $\Psi(r,t) = \Psi f$. Replace this into the general time dependent Schrodinger equation.

$$\begin{aligned}
i\hbar\frac{\partial}{\partial t}(\Psi f) &= \left(-\frac{\hbar^2\nabla^2}{2m}+V\right)\Psi f \\
i\hbar\Psi f\frac{\partial}{\partial t} &= -\frac{\hbar^2\nabla^2}{2m}\Psi f+V\Psi f \\
i\hbar\Psi f^{'} &= -\frac{\hbar^2}{2m}f\Psi^{''}+V\Psi f
\end{aligned}$$

Consolidate the f and Ψ terms giving

$$i\hbar\Psi\frac{f^{'}}{f}=-\frac{\hbar^2}{2m}\Psi^{''}+V\Psi$$

or

$$\boxed{i\hbar\tfrac{f^{'}}{f}=\tfrac{1}{\Psi}[-\tfrac{\hbar^2}{2m}\Psi^{''}+V\Psi]} \tag{20.1}$$

You will note that the left hand side is dependent only on time and that the right hand side is dependent only on position. To be equivalent both sides must equal a constant which we call ϵ. (turns out to be the eigenenergy or eigenvalue)

Left hand side

$$\begin{aligned}
i\hbar\frac{f^{'}}{f} &= \epsilon \\
\frac{f^{'}}{f} &= -\frac{i\epsilon}{\hbar} \\
&\ \text{which we integrate to get} \\
lnf &= -\frac{i\epsilon t}{\hbar}
\end{aligned}$$

The desired time dependent function is

$$\boxed{f(t)=e^{-\frac{i\epsilon t}{\hbar}}} \tag{20.2}$$

Right hand side

$$\begin{aligned}\frac{1}{\Psi}\left[-\frac{\hbar^2}{2m}\Psi^{''}+V\Psi\right] &= \epsilon \\ -\frac{\hbar^2}{2m}\Psi^{''}+V\Psi &= \epsilon\Psi \\ \left(-\frac{\hbar^2}{2m}\nabla^2+V\right)\Psi &= \epsilon\Psi\end{aligned}$$

or

$$\boxed{H_0\Psi=\epsilon\Psi} \tag{20.3}$$

This is our usual eigenvalue and eigenvector problem. Solving this we get ϵ and $\Psi(r)$.

Putting everything together, the general form of the wavefunction is

$$\Psi(r,t)=\Psi(r)f(t)$$

or more explicitly

$$\boxed{\Psi(r,t)=\Psi(r)e^{\frac{-i\epsilon t}{\hbar}}} \tag{20.4}$$

Time dependent perturbation theory now

The basic idea of time-dependent perturbation theory is simple. First understant that if the perturbation (call it V) were absent, the eigenfunctions appropriate to the problem would be given by the equation

$$H^{(0)}\Psi^{(0)}=\epsilon^{(0)}\Psi^{(0)}$$

If the initial state is expanded in terms of these unperturbed eigenfunctions

$$\Psi(t=0)=\sum_n C_n e^{-\frac{i\epsilon_n^{(0)}t}{\hbar}}\Psi_n^{(0)}(r)$$

where C_n is a constant, then in the absence of a perturbation we would have for all times

$$\Psi(t>0)=\sum_n C_n e^{-\frac{i\epsilon_n^{(0)}t}{\hbar}}\Psi_n^{(0)}(r)$$

where again C_n is a constant.

If the perturbation is present however, the above linear combination is no longer a valid solution to the Schrodinger equation.

But we can still express whatever true solution exists as a linear combination of the un-perturbed zero order wavefunctions provided that the coefficients are now time dependent.

$$\begin{aligned}\Psi(r,t) &= \sum_n C_n(t) e^{-\frac{i\epsilon_n^{(0)} t}{\hbar}} \Psi_n^{(0)}(r) \\ &= \sum_n C_n(t) \Psi_n(r,t)\end{aligned}$$

So let's go ahead and start deriving some results of the time dependent perturbation theory.

Plug our time dependent form of the wavefunction back into the general time dependent Schrodinger equation.

$$i\hbar \frac{d\Psi(r,t)}{dt} = H\Psi(r,t)$$

where $H = H^{(0)} + V(t)$ or $H^{(0)} + H^{(1)}(t)$. Use whatever notation that suits you. We then have

$$i\hbar \frac{d\Psi(r,t)}{dt} = (H^{(0)} + H^{(1)})\Psi(r,t)$$

Ok since the notation gets wild, we're going to drop the (t) in $C_n(t)$. Just understand that the time dependence is implied. Furthermore, just work with $\Psi_n(r,t)$ instead of the full expression.

$$\begin{aligned}[H^{(0)} + H^{(1)}] \sum_n C_n \Psi_n(r,t) &= i\hbar \frac{d}{dt} [\sum_n C_n \Psi_n(r,t)] \\ H^{(0)} \sum_n C_n \Psi_n(r,t) + H^{(1)} \sum_n C_n \Psi_n(r,t) &= i\hbar \frac{d}{dt} [\sum_n C_n \Psi_n(r,t)]\end{aligned}$$

Expand the right hand side using the Chain rule.

$$\begin{aligned} & H^{(0)}\sum_n C_n\Psi_n(r,t) + H^{(1)}\sum_n C_n\Psi_n(r,t) \\ = \; & i\hbar[\sum_n C_n\frac{d\Psi_n(r,t)}{dt} + \sum_n \frac{dC_n}{dt}\Psi_n(r,t)] \\ & H^{(0)}\sum_n C_n\Psi_n(r,t) + H^{(1)}\sum_n C_n\Psi_n(r,t) \\ = \; & i\hbar\sum_n C_n\frac{d\Psi_n(r,t)}{dt} + i\hbar\sum_n \frac{dC_n}{dt}\Psi_n(r,t) \end{aligned}$$

The first terms on the left and right side of the last expression will cancel. To illustrate let $n = 1$ for example.

$$\begin{aligned} H^{(0)}C_1\Psi_1(r,t) &= i\hbar C_1\frac{d\Psi_1(r,t)}{dt} \\ H^{(0)}C_1\Psi_1(r)e^{-\frac{i\epsilon_1^{(0)}t}{\hbar}} &= i\hbar C_1\Psi_1(r)e^{-\frac{i\epsilon_1^{(0)}t}{\hbar}}\left(-\frac{i\epsilon_1^{(0)}}{\hbar}\right) \\ \text{cancel common terms} & \\ H^{(0)}\Psi_1(r) &= \epsilon_1^{(0)}\Psi_1(r) \end{aligned}$$

which is our favorite eigenvalue and eigenvector relation. The sample applies for all n so that we are left with

$$\boxed{H^{(1)}\sum_n C_n\Psi_n(r,t) = i\hbar\sum_n \frac{dC_n}{dt}\Psi_n(r,t)} \tag{20.5}$$

Now we desire to solve this expression for the time dependent coefficients of some state say k.

Multiply both sides by $\Psi_k^{(0)*}(r)$ and recall that all states $n \neq k$ of the same basis are orthogonal.

$$\begin{aligned} \Psi_k^{(0)*}(r)H^{(1)}\sum_n C_n\Psi_n(r,t) &= i\hbar\sum_n \frac{dC_n}{dt}\Psi_k^{(0)*}(r)\Psi_n(r,t) \\ \sum_n C_n\Psi_k^{(0)*}(r)H^{(1)}\Psi_n(r,t) &= i\hbar\sum_n \frac{dC_n}{dt}\Psi_k^{(0)*}(r)\Psi_n(r,t) \\ \sum_n C_n\Psi_k^{(0)*}(r)H^{(1)}\Psi_n^{(0)}(r)e^{-\frac{i\epsilon_n^{(0)}t}{\hbar}} &= i\hbar\sum_n \frac{dC_n}{dt}\Psi_k^{(0)*}(r)\Psi_n^{(0)}(r)e^{-\frac{i\epsilon_n^{(0)}}{\hbar}} \\ & \quad \text{where } n = k \text{ on right side} \\ \sum_n C_n < k|H^{(1)}|n > e^{-\frac{i\epsilon_n^{(0)}t}{\hbar}} &= i\hbar\frac{dC_n}{dt}e^{-\frac{i\epsilon_k^{(0)}t}{\hbar}} \end{aligned}$$

Multiply both sides by $e^{\frac{i\epsilon_k^{(0)}t}{\hbar}}$ to simplify.

$$\begin{aligned}
\sum_n C_n < k|H^{(1)}|n > e^{-\frac{i\epsilon_n^{(0)}t}{\hbar}} e^{\frac{i\epsilon_k^{(0)}t}{\hbar}} &= i\hbar\frac{dC_k}{dt} \\
\sum_n C_n < k|H^{(1)}|n > e^{\frac{i(\epsilon_k^{(0)}-\epsilon_n^{(0)})t}{\hbar}} &= i\hbar\frac{dC_k}{dt}
\end{aligned}$$

Let $\omega_{kn} = \frac{\epsilon_k^{(0)}-\epsilon_n^{(0)}}{\hbar}$ since $\Delta\epsilon = \hbar\omega$ yielding

$$\sum_n C_n < k|H^{(1)}|n > e^{i\omega_{kn}t} = i\hbar\frac{dC_k}{dt}$$

or better yet

$$\boxed{i\hbar\frac{dC_k}{dt} = \sum_n C_n < k|H^{(1)}|n > e^{i\omega_{kn}t}} \qquad (20.6)$$

This is basically a system of simultaneous linear differential equations.

In matrix notation

$$i\hbar\frac{d}{dt}\begin{pmatrix} C_1 \\ C_2 \\ C_3 \\ \dots \\ C_k \end{pmatrix} = \begin{pmatrix} V_{11} & V_{12}e^{i\omega_{12}t} & \dots \\ V_{21}e^{-i\omega_{12}t} & V_{22} & \dots \\ \dots & \dots & \dots \\ \dots & \dots & \dots \\ \dots & \dots & \dots \end{pmatrix} \begin{pmatrix} C_1 \\ C_2 \\ C_3 \\ \dots \\ \dots \end{pmatrix}$$

Now what? This expression is pretty tough to solve. So to overcome this problem you apply time dependent perturbation theory (which is basically making some assumptions about the size of the perturbation and in turn what $C_1, C_2, C_3, \dots$ are).

To illustrate, suppose the system starts out in state 1. Then

$$\begin{aligned}
C_1(t=0) &= 1 \\
C_2(t=0) &= 0 \\
C_3(t=0) &= 0
\end{aligned}$$

and so forth.

If there are no perturbations, then the system stays in state 1 forever.

Our zeroth order approximation is therefore

$$\begin{aligned} C_1(t) &= 1 \\ C_2(t) &= 0 \\ C_3(t) &= 0 \\ &\cdots \\ C_n(t) &= 0 \end{aligned}$$

To get our first order approximation insert these zeroth order values into our matrix yielding

$$\begin{aligned} i\hbar\frac{dC_k}{dt} &= C_{n=1} < k|H^{(1)}|n=1 > e^{i\omega_{kn=1}t} \\ \frac{dC_k}{dt} &= \frac{1}{i\hbar}C_{n=1} < k|H^{(1)}|n=1 > e^{i\omega_{kn=1}t} \\ & \text{where } c_{n=1} \approx 1 \end{aligned}$$

yielding

$$\boxed{C_k(t) = \frac{1}{i\hbar}\int_0^t < k|H^{(1)}|n=1 > e^{i\omega_{kn=1}t'}dt'} \tag{20.7}$$

Note however that when integrating $\frac{dC_k}{dt}$ there is actually a constant of integration that comes out.

$$C_k(t) = const + \frac{1}{i\hbar}\int_0^t < k|H^{(1)}|n > e^{i\omega_{kn}t'}dt'$$

where $const = C_k(t=0) = \delta_{kn}$. Replacing this into the above expression gives

$$C_k(t) = C_k(0) + \frac{1}{i\hbar}\int_0^t < k|H^{(1)}|n > e^{i\omega_{kn}t'}dt'$$

or your standard textbook expression

$$\boxed{C_k(t) = \delta_{kn} + \frac{1}{i\hbar}\int_0^t < k|H^{(1)}|n > e^{i\omega_{kn}t'}dt'} \tag{20.8}$$

Summary

$$\boxed{C_k^{(0)}(t) = \delta_{kn}} \tag{20.9}$$

$$\boxed{C_k^{(1)}(t) = \frac{1}{i\hbar}\int_0^t < k|H^{(1)}|n > e^{i\omega_{kn}t'}dt'} \tag{20.10}$$

Two level system, sinusoidal perturbation, Schrodinger representation

Let's illustrate our results with a more concrete example and for simplicity keep it to two levels (a two level system, TLS).

Recall that our time dependent Schrodinger equation is

$$\begin{aligned} i\hbar\frac{d}{dt}\Psi(r,t) &= H\Psi(r,t) \\ & \quad \text{where } H = H^{(0)} + H^{(1)} \\ i\hbar\frac{d}{dt}\Psi(r,t) &= (H^{(0)} + H^{(1)})\Psi(r,t) \end{aligned}$$

Now recall that a general solution to this time dependent Schrodinger equation can be expressed as a linear combination of the unperturbed zero order wavefunctions, provided time dependent coefficients.

$$\boxed{\Psi(r,t) = C_1(t)\Psi_1(r,t) + C_2(t)\Psi_2(r,t)} \qquad (20.11)$$

where

$$\begin{aligned} \Psi_1(r,t) &= \Psi_1(r)e^{-\frac{i\epsilon_1^{(0)}t}{\hbar}} \\ \Psi_2(r,t) &= \Psi_2(r)e^{-\frac{i\epsilon_2^{(0)}t}{\hbar}} \end{aligned}$$

Now let's be more specific with what $H^{(1)}(t)$ looks like. We want to consider the interaction of a molecule with dipole moment μ with light where the electric field of light can be written as

$$\epsilon = \epsilon_0 cos 2\pi\nu t$$

where ν is the frequency of the radiation. Alternatively

$$\boxed{\epsilon = \epsilon_0 cos\omega t} \qquad (20.12)$$

This is going to be our sinusoidal perturbation. You can see that it will oscillate periodically with time.

The interaction between a molecule's dipole moment and the electric field is then

$$H^{(1)} = -\mu \cdot \epsilon$$

$$\boxed{H^{(1)} = -\mu \cdot \epsilon_0 cos\omega t} \qquad (20.13)$$

Such that

$$\boxed{H = H^{(0)} - \mu \cdot \epsilon_0 cos\omega t} \tag{20.14}$$

We are now going to re-derive our previous expression for the coefficients. Insert $\Psi(r,t)$ into the Schrodinger equation. Also for shorthand let the time dependence of the coefficients be understood $C_1(t) \rightarrow C_1$ and $C_2(t) \rightarrow C_2$.

$$\begin{aligned}
& i\hbar\frac{d}{dt}[C_1\Psi_1(r,t) + C_2\Psi_2(r,t)] \\
= \quad & (H^{(0)} + H^{(1)})[C_1\psi_1(r,t) + C_2\Psi_2(r,t)] \\
\\
& i\hbar\frac{d}{dt}(C_1\Psi_1(r,t)) + i\hbar\frac{d}{dt}(C_2\Psi_2(r,t)) \\
= \quad & (H^{(0)} + H^{(1)})[C_1\Psi(r,t) + C_2\Psi_2(r,t)] \\
\\
& i\hbar C_1\frac{d\Psi_1(r,t)}{dt} + i\hbar\Psi_1(r,t)\frac{dC_1}{dt} + i\hbar C_2\frac{d\Psi_2(r,t)}{dt} + i\hbar\Psi_2(r,t)\frac{dC_2}{dt} \\
= \quad & H^{(0)}(C_1\Psi_1(r,t) + C_2\Psi_2(r,t)) + H^{(1)}(C_1\Psi_1(r,t) + C_2\Psi_2(r,t)) \\
\\
& C_1 i\hbar\frac{d\Psi_1(r,t)}{dt} + C_2 i\hbar\frac{d\Psi_2(r,t)}{dt} + i\hbar\Psi_1(r,t)\frac{dC_1}{dt} + i\hbar\Psi_2(r,t)\frac{dC_2}{dt} \\
= \quad & C_1H^{(0)}\Psi_1(r,t) + C_2H^{(0)}\Psi_2(r,t) + C_1H^{(1)}\Psi_1(r,t) + C_2H^{(1)}\Psi_2(r,t)
\end{aligned}$$

We've seen previously that the first terms on either side of the last equation will cancel since they are equivalent.

$$\begin{aligned}
H^{(0)}\Psi_1(r,t) &= i\hbar\frac{d\Psi_1(r,t)}{dt} \\
H^{(0)}\Psi_2(r,t) &= i\hbar\frac{d\Psi_2(r,t)}{dt}
\end{aligned}$$

leaving

$$\boxed{i\hbar\Psi_1(r,t)\tfrac{dC_1}{dt} + i\hbar\Psi_2(r,t)\tfrac{dC_2}{dt} = C_1H^{(1)}\Psi_1(r,t) + C_2H^{(1)}\Psi_2(r,t)} \tag{20.15}$$

Now like before, multiply both sides by $\Psi_2^{(0)*}(r)$ and integrate.

$$\begin{aligned} & i\hbar\Psi_2^{(0)*}(r)\Psi_1(r,t)\frac{dC_1}{dt} + i\hbar\Psi_2^{(0)*}(r)\Psi_2(r,t)\frac{dC_2}{dt} \\ = & \ C_1\Psi_2^{(0)*}(r)H^{(1)}\Psi_1(r,t) + C_2\Psi_2^{(0)*}(r)H^{(1)}\Psi_2(r,t) \end{aligned}$$

$$\begin{aligned} & i\hbar < 2|1 > e^{-\frac{i\epsilon_1^{(0)}t}{\hbar}}\frac{dC_1}{dt} + i\hbar < 2|2 > e^{-\frac{i\epsilon_2^{(0)}t}{\hbar}}\frac{dC_2}{dt} \\ = & \ C_1 < 2|H^{(1)}|1 > e^{-\frac{i\epsilon_1^{(0)}t}{\hbar}} + C_2 < 2|H^{(1)}|2 > e^{-\frac{i\epsilon_2^{(0)}t}{\hbar}} \end{aligned}$$

$$\begin{aligned} i\hbar e^{-\frac{i\epsilon_2^{(0)}t}{\hbar}}\frac{dC_2}{dt} &= C_1 < 2|H^{(1)}|1 > e^{-\frac{i\epsilon_1^{(0)}t}{\hbar}} + C_2 < 2|H^{(1)}|2 > e^{-\frac{i\epsilon_2^{(0)}t}{\hbar}} \\ & \text{multiply both sides by } e^{\frac{i\epsilon_2^{(0)}t}{\hbar}} \\ i\hbar\frac{dC_2}{dt} &= C_1 < 2|H^{(1)}|1 > e^{\frac{i(\epsilon_2^{(0)}-\epsilon_1^{(0)})t}{\hbar}} + C_2 < 2|H^{(1)}|2 > \end{aligned}$$

as before let $\omega_{21} = \frac{\epsilon_2^{(0)}-\epsilon_1^{(0)}}{\hbar}$. The exact expression we get then is

$$\boxed{i\hbar\frac{dC_2}{dt} = C_1 < 2|H^{(1)}|1 > e^{i\omega_{21}t} + C_2 < 2|H^{(1)}|2 >} \tag{20.16}$$

Now we invoke time dependent perturbation theory and assume that since $H^{(1)}$ is small

$$\begin{aligned} C_1(t) &\simeq 1 \\ C_2(t) &\simeq 0 \end{aligned}$$

giving

$$\boxed{i\hbar\frac{dC_2}{dt} =< 2|H^{(1)}|1 > e^{i\omega_{21}t}} \tag{20.17}$$

What now? Well, we haven't really dealt with $H^{(1)}$ yet. Recall that

$$H^{(1)} = -\mu \cdot \epsilon_0 cos\omega t$$

For convenience, choose the z direction

$$H_z^{(1)} = -\mu\epsilon_0 cos\omega t$$

or

$$\boxed{H_z^{(1)} = -\mu_z\epsilon_0\left(\tfrac{e^{i\omega t}+e^{-i\omega t}}{2}\right)} \tag{20.18}$$

Ok, let's throw this into our previous expression and see what happens.

$$\begin{aligned}
i\hbar\frac{dC_2}{dt} &= <2|-\frac{\mu_z\epsilon_0}{2}(e^{i\omega t}+e^{-i\omega t})|1> e^{i\omega_{21}t} \\
i\hbar\frac{dC_2}{dt} &= -\frac{\epsilon_0}{2}<2|\mu_z(e^{i\omega t}+e^{-i\omega t})|1> e^{i\omega_{21}t} \\
i\hbar\frac{dC_2}{dt} &= -\frac{\epsilon_0}{2}<2|\mu_z|1>\left(e^{i\omega t+i\omega_{21}t}+e^{-i\omega t+i\omega_{21}t}\right)
\end{aligned}$$

The term $<2|\mu_z|1>$ is the transition dipole moment.

$$\begin{aligned}
i\hbar\frac{dC_2}{dt} &= -\frac{\epsilon_0}{2}<2|\mu_z|1>\left(e^{i(\omega+\omega_{21})t}+e^{-i(\omega-\omega_{21}t)}\right) \\
\frac{dC_2}{dt} &= \frac{i\epsilon_0}{2\hbar}<2|\mu_z|1>\left(e^{i(\omega+\omega_{21})t}+e^{-i(\omega-\omega_{21})t}\right)
\end{aligned}$$

Integrate this to find $C_2(t)$ but before we do this, let's flip back to ϵ notation so that our final expression will be consistent with everyone elses.

$$\frac{dC_2}{dt} = \frac{i\epsilon_0}{2\hbar}<2|\mu_z|1>\left(e^{i\frac{\hbar\omega+\hbar\omega_{21}}{\hbar}t}+e^{-i\frac{\hbar\omega-\hbar\omega_{21}}{\hbar}t}\right)$$

where $\hbar\omega = h\nu$ and $\hbar\omega_{21} = \hbar\omega_2 - \hbar\omega_1 = \epsilon_2 - \epsilon_1$

$$\frac{dC_2}{dt} = \frac{i\epsilon_0}{2\hbar}<2|\mu_z|1>\left(e^{i\frac{h\nu+(\epsilon_2-\epsilon_1)}{\hbar}t}+e^{-i\frac{h\nu-\epsilon_2+\epsilon_1}{\hbar}t}\right)$$

$$\boxed{\tfrac{dC_2}{dt} = \tfrac{i\epsilon_0}{2\hbar}<2|\mu_z|1>\left(e^{i\frac{(\epsilon_2-\epsilon_1+h\nu)}{\hbar}t}+e^{i\frac{(\epsilon_2-\epsilon_1-h\nu)}{\hbar}t}\right)} \tag{20.19}$$

Now integrate this to get $C_2(t)$. Remember that when you integrate $\frac{dC_2}{dt}$ you get an additional constant of integration which is $C_2(0)$.

$$\begin{aligned}
C_2(t) &= C_2(0)+\frac{i\epsilon_0<2|\mu_z|1>}{2\hbar}\int_0^t e^{\frac{i(\epsilon_2-\epsilon_1+h\nu)t'}{\hbar}}+e^{\frac{i(\epsilon_2-\epsilon_1-h\nu)t'}{\hbar}}dt' \\
&\quad \text{where } C_2(0) = \delta_{12} \\
C_2(t) &= \delta_{12}+\frac{i\epsilon_0<2|\mu_z|1>}{2\hbar}\int_0^t e^{\frac{i(\epsilon_2-\epsilon_1+h\nu)t'}{\hbar}}+e^{\frac{i(\epsilon_2-\epsilon_1-h\nu)t'}{\hbar}}dt'
\end{aligned}$$

but since states $1 \neq 2$ we are left in practice with the 1st order contribution. So let's just work with it.

$$\boxed{C_2^{(1)}(t) = \frac{i\epsilon_0 < 2|\mu_z|1 >}{2\hbar}\int_0^t e^{\frac{i(\epsilon_2-\epsilon_1+h\nu)t'}{\hbar}} + e^{\frac{i(\epsilon_2-\epsilon_1-h\nu)t'}{\hbar}} dt'} \tag{20.20}$$

So go on and integrate this expression.

$$C_2^{(1)}(t) = \frac{\epsilon_0 < 2|\mu_z|1 >}{2}\left[\frac{(e^{\frac{i(\epsilon_2-\epsilon_1+h\nu)t}{\hbar}} - 1)\hbar}{i(\epsilon_2-\epsilon_1+h\nu)} + \frac{(e^{\frac{i(\epsilon_2-\epsilon_1-h\nu)t}{\hbar}} - 1)\hbar}{i(\epsilon_2-\epsilon_1-h\nu)}\right]$$

or

$$\boxed{C_2^{(1)}(t) = \frac{\epsilon_0 < 2|\mu_z|1 >}{2}\left[\frac{(e^{\frac{i(\epsilon_2-\epsilon_1+h\nu)t}{\hbar}} - 1)}{(\epsilon_2-\epsilon_1+h\nu)} + \frac{(e^{\frac{i(\epsilon_2-\epsilon_1-h\nu)t}{\hbar}} - 1)}{(\epsilon_2-\epsilon_1-h\nu)}\right]} \tag{20.21}$$

Now at this point, another approximation is made here.

You have two terms. The one with $(\epsilon_2 - \epsilon_1 - h\nu)$ in the denominator is called the resonant term. The one with $(\epsilon_2 - \epsilon_1 + h\nu)$ is called the non-resonant term.

When $h\nu = (\epsilon_2 - \epsilon_1)$ the resonant term will dominate. Under this resonance condition where the monochromatic light energy equals the energy difference between states 1 and 2 you get

$$\boxed{C_2^{(1)}(t) \simeq \frac{\epsilon_0 < 2|\mu_z|1 >}{2}\left[\frac{e^{\frac{i(\epsilon_2-\epsilon_1-h\nu)t}{\hbar}} - 1}{(\epsilon_2-\epsilon_1-h\nu)}\right]} \tag{20.22}$$

Note that this approximation is also called the "Rotating Wave Approximation".

Since we like math, let's keep simplifying. Extract out $e^{\frac{i(\epsilon_2-\epsilon_1-h\nu)t}{2\hbar}}$

$$\begin{aligned} C_2^{(1)}(t) &\simeq \frac{\epsilon_0 < 2|\mu_z|1 >}{2} e^{\frac{i(\epsilon_2-\epsilon_1-h\nu)t}{2\hbar}} \left(\frac{e^{\frac{i(\epsilon_2-\epsilon_1-h\nu)t}{2\hbar}} - e^{\frac{-i(\epsilon_2-\epsilon_1-h\nu)t}{2\hbar}}}{\epsilon_2-\epsilon_1-h\nu}\right) \\ C_2^{(1)}(t) &\simeq \frac{i\epsilon_0 < 2|\mu_z|1 >}{(\epsilon_2-\epsilon_1-h\nu)} e^{\frac{i(\epsilon_2-\epsilon_1-h\nu)t}{2\hbar}} \left(\frac{e^{\frac{i(\epsilon_2-\epsilon_1-h\nu)t}{2\hbar}} - e^{\frac{-i(\epsilon_2-\epsilon_1-h\nu)t}{2\hbar}}}{2i}\right) \end{aligned}$$

resulting in

$$\boxed{C_2^{(1)}(t) \simeq \frac{i\epsilon_0 < 2|\mu_z|1 >}{(\epsilon_2-\epsilon_1-h\nu)} e^{\frac{i(\epsilon_2-\epsilon_1-h\nu)t}{2\hbar}} sin\left(\frac{\epsilon_2-\epsilon_1-h\nu}{2\hbar}\right)t} \tag{20.23}$$

Ok, let's keep going. Recall that the probability of being in a particular state k is basically

$$P_k = |C_k|^2$$

Therefore the transition probability into the final state 2 is

$$\begin{aligned} P_2 &= |C_2(t)|^2 \\ &= \frac{\epsilon_0^2 | < 2|\mu_z|1 > |^2}{(\epsilon_2 - \epsilon_1 - h\nu)^2} sin^2 \left(\frac{\epsilon_2 - \epsilon_1 - h\nu}{2\hbar} \right) t \end{aligned}$$

The final transition probability into state 2 is

$$\boxed{P_2 = \epsilon_0^2 | < 2|\mu_z|1 > |^2 \left(\frac{sin^2(\frac{\epsilon_2 - \epsilon_1 - h\nu)t}{2\hbar})}{(\epsilon_2 - \epsilon_1 - h\nu)^2} \right)} \qquad (20.24)$$

Note that P_2 is $P_2(h\nu, t)$. It depends on both time and frequency. Finally, more generally, if you didn't take the time dependent perturbation theory approach and $C_1(t)$ is not necessarily 1 and $C_2(t)$ is not necessarily 0, you can solve for $C_1(t)$ and $P_1(h\nu, t)$ as well as $C_2(t)$ and $P_2(h\nu, t)$

Starting with

$$\begin{aligned} & i\hbar\Psi_1(r,t)\frac{dC_1}{dt} + i\hbar\Psi_2(r,t)\frac{dC_2}{dt} \\ = \; & C_1 H^{(1)}\Psi_1(r,t) + C_2 H^{(1)}\Psi_2(r,t) \end{aligned}$$

Multiply both sides by $\Psi_1^{(0)*}(r)$ and integrate.

$$\begin{aligned} & i\hbar < 1|1 > e^{\frac{-i\epsilon_1^{(0)}t}{\hbar}} \frac{dC_1}{dt} + i\hbar < 1|2 > e^{\frac{-i\epsilon_2^{(0)}t}{\hbar}} \frac{dC_2}{dt} \\ = \; & C_1 < 1|H^{(1)}|1 > e^{\frac{-i\epsilon_1^{(0)}t}{\hbar}} + C_2 < 1|H^{(1)}|2 > e^{\frac{-i\epsilon_2^{(0)}t}{\hbar}} \end{aligned}$$

$$i\hbar e^{\frac{-i\epsilon_1^{(0)}t}{\hbar}} \frac{dC_1}{dt} = C_1 < 1|H^{(1)}|1 > e^{\frac{-i\epsilon_1^{(0)}t}{\hbar}} + C_2 < 1|H^{(1)}|2 > e^{\frac{-i\epsilon_2^{(0)}t}{\hbar}}$$

Multiply through by $e^{\frac{i\epsilon_1^{(0)}t}{\hbar}}$ to yield

$$\boxed{i\hbar\frac{dC_1}{dt} = C_1 < 1|H^{(1)}|1 > + C_2 < 1|H^{(1)}|2 > e^{\frac{-i(\epsilon_2^{(0)} - \epsilon_1^{(0)})t}{\hbar}}} \qquad (20.25)$$

Likewise we found before that

$$\boxed{i\hbar\frac{dC_2}{dt} = C_1 < 2|H^{(1)}|1 > e^{i\omega_{21}t} + C_2 < 2|H^{(1)}|2 >} \tag{20.26}$$

Putting it all together in matrix form we get

$$\boxed{i\hbar\frac{d}{dt}\begin{pmatrix} C_1 \\ C_2 \end{pmatrix} = \begin{pmatrix} < 1|H^{(1)}|1 > & < 1|H^{(1)}|2 > e^{-i\omega_{21}t} \\ < 2|H^{(1)}|1 > e^{i\omega_{21}t} & < 2|H^{(1)}|2 > \end{pmatrix}\begin{pmatrix} C_1 \\ C_2 \end{pmatrix}} \tag{20.27}$$

You are now forced to solve this explicitly (as we will do in the next section).

Chapter 21

Rabi Solutions, Schrodinger Representation

Rather than do time dependent perturbation theory, let's solve the two level system considered previously exactly. This will help motivate why the perturbation theory approach is convenient.

We have from before where $C_1 = C_1(t)$ and $C_2 = C_2(t)$

$$\begin{aligned} i\hbar\frac{dC_1}{dt} &= C_1 < 1|H^{(1)}|1 > + C_2 < 1|H^{(1)}|2 > e^{-i\omega_{21}t} \\ i\hbar\frac{dC_2}{dt} &= C_1 < 2|H^{(1)}|1 > e^{i\omega_{21}t} + C_2 < 2|H^{(1)}|2 > \end{aligned}$$

Now suppose that $< 1|H^{(1)}|1 >=< 2|H^{(1)}|2 >= 0$ at all times. This condition is satisfied by many common types of perturbations.

Now we are left with

$$\boxed{i\hbar\tfrac{dC_1}{dt} = C_2 < 1|H^{(1)}|2 > e^{-i\omega_{21}t}} \tag{21.1}$$

$$\boxed{i\hbar\tfrac{dC_2}{dt} = C_1 < 2|H^{(1)}|1 > e^{i\omega_{21}t}} \tag{21.2}$$

Note that we are not invoking a time dependent perturbation theory approximation here.

Let's introduce $H^{(1)} = -\mu_z \epsilon_0 cos\omega t$ our sinusoidal perturbation now and get more explicit expressions just like we did last time.

$$\begin{aligned}
i\hbar\frac{dC_1}{dt} &= C_2 < 1| - \mu_z\epsilon_0 cos\omega t|2 > e^{-i\omega_{21}t} \\
i\hbar\frac{dC_1}{dt} &= -C_2\epsilon_0 < 1|\mu_z|2 > e^{-i\omega_{21}t}cos\omega t \\
i\hbar\frac{dC_1}{dt} &= -C_2\epsilon_0 < 1|\mu_z|2 > e^{-i\omega_{21}t}\left(\frac{e^{i\omega t}+e^{-i\omega t}}{2}\right)
\end{aligned}$$

leaving

$$\boxed{i\hbar\frac{dC_1}{dt} = -\frac{C_2\epsilon_0}{2} < 1|\mu_z|2 > (e^{-i(\omega_{21}-\omega)t} + e^{-i(\omega_{21}+\omega)t})} \tag{21.3}$$

Now for the other expression

$$\begin{aligned}
i\hbar\frac{dC_2}{dt} &= C_1 < 2| - \mu_z\epsilon_0 cos\omega t|1 > e^{1\omega_{21}t} \\
i\hbar\frac{dC_2}{dt} &= -C_1\epsilon_0 < 2|\mu_z|1 > cos\omega t e^{i\omega_{21}t} \\
i\hbar\frac{dC_2}{dt} &= -\frac{C_1\epsilon_0}{2} < 2|\mu_z|1 > e^{i\omega_{21}t}(e^{i\omega t}+e^{-i\omega t})
\end{aligned}$$

leaving

$$\boxed{i\hbar\frac{dC_2}{dt} = -\frac{C_1\epsilon_0}{2} < 2|\mu_z|1 > (e^{i(\omega_{21}+\omega)t} + e^{i(\omega_{21}+\omega)t})} \tag{21.4}$$

Summary

$$\boxed{i\hbar\frac{dC_1}{dt} = -\frac{C_2\epsilon_0}{2} < 1|\mu_z|2 > (e^{-i(\omega_{21}-\omega)t} + e^{-i(\omega_{21}+\omega)t})} \tag{21.5}$$

$$\boxed{i\hbar\frac{dC_2}{dt} = -\frac{C_1\epsilon_0}{2} < 2|\mu_z|1 > (e^{i(\omega_{21}+\omega)t} + e^{i(\omega_{21}+\omega)t})} \tag{21.6}$$

Now to simplify things, let's just look ahead and see that the Rotating Wave Approximation allows us to drop some terms near resonance. Specifically $e^{-i(\omega_{21}+\omega)t}$ in the 1st expression for $\frac{dC_1}{dt}$ and $e^{i(\omega_{21}+\omega)t}$ in the second expression for $\frac{dC_2}{dt}$

This leaves us with

$$\boxed{i\hbar\frac{dC_1}{dt} = -\frac{C_2\epsilon_0}{2} < 1|\mu_z|2 > e^{-i(\omega_{21}+\omega)t}} \tag{21.7}$$

$$\boxed{i\hbar\frac{dC_2}{dt} = -\frac{C_1\epsilon_0}{2} < 2|\mu_z|1 > e^{i(\omega_{21}-\omega)t}} \tag{21.8}$$

Ok, since we're not doing time dependent perturbation theory how do we go about solving this system of coupled differential equations. There are several ways, among them Laplace transforms. But here we will simply end up substituting one expression into another.

Take the second derivative of the second expression (dont forget that $C_1 = C_1(t)$)

$$\begin{aligned}
i\hbar\frac{d^2C_2}{dt^2} &= -\frac{\epsilon_0}{2} < 2|\mu_z|1 > \frac{d}{dt}[C_1 e^{i(\omega_{21}-\omega)t}] \\
i\hbar\frac{d^2C_2}{dt^2} &= -\frac{\epsilon_0}{2} < 2|\mu_z|1 > [C_1 i(\omega_{21}-\omega)e^{i(\omega_{21}-\omega)t} + e^{i(\omega_{21}-\omega)t}\frac{dC_1}{dt}] \\
i\hbar\frac{d^2C_2}{dt^2} &= -\frac{\epsilon_0}{2} < 2|\mu_z|1 > e^{i(\omega_{21}-\omega)t}[iC_1(\omega_{21}-\omega) + \frac{dC_1}{dt}]
\end{aligned}$$

where we know that $i\hbar\frac{dC_1}{dt} = -\frac{C_2\epsilon_0}{2} < 1|\mu_z|2 > e^{-i(\omega_{21}-\omega)t}$. We replace $\frac{dC_1}{dt} = \frac{iC_2\epsilon_0}{2\hbar} < 1|\mu_z|2 > e^{-i(\omega_{21}-\omega)t}$ into the above expression resulting in

$$\begin{aligned}
i\hbar\frac{d^2C_2}{dt^2} &= -\frac{\epsilon_0}{2} < 2|\mu_z|1 > e^{i(\omega_{21}-\omega)t}[iC_1(\omega_{21}-\omega) + \frac{iC_2\epsilon_0}{2\hbar} < 1|\mu_z|2 > e^{-i(\omega_{21}-\omega)t}] \\
\frac{d^2C_2}{dt^2} &= -\frac{\epsilon_0}{2\hbar} < 2|\mu_z|1 > e^{i(\omega_{21}-\omega)t}[C_1(\omega_{21}-\omega) + \frac{C_2\epsilon_0^2}{2\hbar} < 1|\mu_z|2 > e^{-i(\omega_{21}-\omega)t}] \\
\frac{d^2C_2}{dt^2} &= -\frac{\epsilon_0}{2\hbar} < 2|\mu_z|1 > (\omega_{21}-\omega)C_1 e^{i(\omega_{21}-\omega)t} - \frac{C_2\epsilon_0^2}{4\hbar^2}| < 1|\mu_z|2 > |^2
\end{aligned}$$

where from $i\hbar\frac{dC_2}{dt} = -C_1\frac{\epsilon_0}{2} < 2|\mu_z|1 > e^{i(\omega_{21}-\omega)t}$ one gets $C_1 = -\frac{2i\hbar}{\epsilon_0}(\frac{1}{<2|\mu_z|1>})e^{-i(\omega_{21}-\omega)t}\frac{dC_2}{dt}$. Plug this in and keep evaluating

$$\frac{d^2C_2}{dt^2} = i(\omega_{21}-\omega)\frac{dC_2}{dt} - \frac{C_2\epsilon_0^2}{4\hbar^2}| < 1|\mu_z|2 > |^2$$

or

$$\boxed{\frac{d^2C_2}{dt^2} + i(\omega-\omega_{21})\frac{dC_2}{dt} + \frac{C_2\epsilon_0^2}{4\hbar^2}| < 1|\mu_z|2 > |^2 = 0} \tag{21.9}$$

This is now a second order homogeneous differential equation.

In general, the solutions will be exponential-like $C_2 \propto e^{\lambda t}$ but λ may be real or imaginary. Let's just say λ is imaginary to save time. Assume a solution of the form $C_2 = e^{i\lambda}t$ and replace this into our second order differential equation.

$$\begin{aligned}
\frac{dC_2}{dt} &= i\lambda e^{i\lambda t} \\
\frac{d^2C_2}{dt^2} &= i\lambda(i\lambda)e^{i\lambda t} = -\lambda^2 e^{i\lambda t}
\end{aligned}$$

Therefore

$$\frac{d^2C_2}{dt^2} + i(\omega - \omega_{21})\frac{dC_2}{dt} + \frac{C_2\epsilon_0^2}{4\hbar^2}| < 1|\mu_z|2 > |^2 = 0$$

becomes

$$\begin{aligned} -\lambda^2 e^{i\lambda t} + i(\omega-\omega_{21})i\lambda e^{i\lambda t} + e^{i\lambda t}\frac{\epsilon_0^2}{4\hbar^2}| < 1|\mu_z|2 > |^2 &= 0 \\ \text{drop } e^{i\lambda t} & \\ -\lambda^2 - (\omega-\omega_{21})\lambda + \frac{\epsilon_0^2| < 1|\mu_z|2 > |^2}{4\hbar^2} &= 0 \end{aligned}$$

leaving us with

$$\boxed{\lambda^2 + \lambda(\omega-\omega_{21}) - \frac{\epsilon_0^2|<1|\mu_z|2>|^2}{4\hbar^2} = 0} \qquad (21.10)$$

This is a quadratic equation whose solutions we all know.

For sake of notational simplicty, call the last constant c and $(\omega-\omega_{21}) = b$.

$$\begin{aligned} \lambda^2 + b\lambda - c = 0 \\ \lambda = \frac{-b \pm \sqrt{b^2+4(1)(c)}}{2(1)} \\ \lambda = \frac{-(\omega-\omega_{21}) \pm \sqrt{(\omega-\omega_{21})^2 + \frac{4\epsilon_0^2|<1|\mu_z|2>|^2}{4\hbar^2}}}{2} \end{aligned}$$

The two roots are then

$$\boxed{\lambda = -\frac{(\omega-\omega_{21})}{2} \pm \frac{1}{2}\sqrt{(\omega-\omega_{21})^2 + \frac{\epsilon_0^2}{\hbar^2}| < 1|\mu_z|2 > |^2}} \qquad (21.11)$$

For even more notational simplicity, let $\Delta = (\omega-\omega_{21})$ and $\Omega = \sqrt{(\omega-\omega_{21})^2 + \frac{\epsilon_0^2|<1|\mu_z|2>|^2}{\hbar^2}}$. This reduces our previous roots to

$$\boxed{\lambda = -\frac{\Delta}{2} \pm \frac{\Omega}{2}} \qquad (21.12)$$

Our general solutions are therefore

$$C_2(t) = Ae^{i(-\frac{\Delta}{2}+\frac{\Omega}{2})t} + Be^{i(-\frac{\Delta}{2}-\frac{\Omega}{2})t}$$

where A and B are constants that are determined by the initial conditions of the problem.

$$\boxed{C_2(t) = e^{-\frac{i\Delta t}{2}}(Ae^{\frac{i\Omega t}{2}} + Be^{\frac{-i\Omega t}{2}})} \qquad (21.13)$$

Ok, now that we have $C_2(t)$, what next? Well, let's go find $C_1(t)$. Take $C_2(t)$ and take its derivative so we can evaluate C_1. First let's rearrange things a little.

$$\begin{aligned} i\hbar\frac{dC_2}{dt} &= -\frac{C_1\epsilon_0}{2} < 2|\mu_z|1 > e^{i(\omega_{21}-\omega)t} \\ C_1 &= \frac{-2i\hbar}{\epsilon_0 < 2|\mu_z|1 >} e^{-i(\omega_{21}-\omega)t}\frac{dC_2}{dt} \end{aligned}$$

where $\Delta = (\omega - \omega_{21})$ giving

$$\boxed{C_1 = -\frac{2i\hbar}{\epsilon_0 < 2|\mu_z|1 >} e^{i\Delta t}\frac{dC_2}{dt}} \tag{21.14}$$

Now plug in $\frac{dC_2}{dt}$ to determine what C_1 is.

$$\begin{aligned} C_2 &= Ae^{\frac{i}{2}(-\Delta+\Omega)t} + Be^{\frac{i}{2}(-\Delta-\Omega)t} \\ \frac{dC_2}{dt} &= A\frac{i}{2}(-\Delta+\Omega)e^{\frac{i}{2}(-\Delta+\Omega)t} + B\frac{i}{2}(-\Delta-\Omega)e^{\frac{i}{2}(-\Delta-\Omega)t} \end{aligned}$$

so that now plugging this into C_1 gives

$$\begin{aligned} C_1 &= -\frac{2i\hbar}{\epsilon + 0 < 2|\mu_z|1 >} e^{i\Delta t}\frac{i}{2}[A(-\Delta+\Omega)e^{\frac{i}{2}(-\Delta+\Omega)t} + B(-\Delta-\Omega)e^{\frac{i}{2}(-\Delta-\Omega)t}] \\ C_1 &= \frac{\hbar e^{\frac{i\Delta t}{2}}}{\epsilon_0 < 2|\mu_z|1 >}[A(-\Delta+\Omega)e^{\frac{i\Omega t}{2}} + B(-\Delta-\Omega)e^{\frac{-i\Omega t}{2}}] \end{aligned}$$

leaving

$$\boxed{C_1 = \frac{\hbar e^{\frac{i\Delta t}{2}}}{\epsilon_0 < 2|\mu_z|1 >}[A(-\Delta+\Omega)e^{\frac{i\Omega t}{2}} + B(-\Delta-\Omega)e^{\frac{-i\Omega t}{2}}]} \tag{21.15}$$

This is our desired expression for $C_1(t)$.

Summary

$$\begin{aligned} C_1(t) &= \frac{\hbar e^{\frac{i\Delta t}{2}}}{\epsilon_0 < 2|\mu_z|1 >}[A(-\Delta+\Omega)e^{\frac{i\Omega t}{2}} + B(-\Delta-\Omega)e^{\frac{-i\Omega t}{2}}] \\ C_2(t) &= e^{-\frac{i\Delta t}{2}}(Ae^{\frac{i\Omega t}{2}} + Be^{\frac{-i\Omega t}{2}}) \end{aligned}$$

Now what, well we still have to solve for the coefficients A and B. Recall that A and B are determined by the initial conditions of the problem.

Suppose at $t = 0$ the system was definitely in state 1. Then $C_1(0) = 1$ and $C_2(0) = 0$.

From this we get

$$\begin{aligned} C_2(0) &= 0 \\ &= A + B \text{ or that } B = -A \end{aligned}$$

Use this in $C_1(0)$ to get

$$\begin{aligned} C_1(0) &= \frac{\hbar}{\epsilon_0 < 2|\mu_z|1>}[A(-\Delta+\Omega) - A(-\Delta-\Omega)] = 1 \\ &= \frac{A\hbar}{\epsilon_0 < 2|\mu_z|1>}[-\Delta+\Omega+\Delta+\Omega] = 1 \\ &= \frac{A\hbar 2\Omega}{\epsilon_0 < 2|\mu_z|1>} = 1 \end{aligned}$$

From this we get our desired coefficients

$$\boxed{A = \frac{\epsilon_0 < 2|\mu_z|1>}{2\hbar\Omega}} \tag{21.16}$$

$$\boxed{B = -\frac{\epsilon_0 < 2|\mu_z|1>}{2\hbar\Omega}} \tag{21.17}$$

Plug these back into our expression for $C_1(t)$ and $C_2(t)$.

$$\begin{aligned} C_1(t) &= \frac{\hbar e^{\frac{i\Delta t}{2}}}{\epsilon_0 < 2|\mu_z|1>}\left[\frac{\epsilon_0 < 2|\mu_z|1>}{2\hbar\Omega}(-\Delta+\Omega)e^{\frac{i\Omega t}{2}} - \frac{\epsilon_0 < 2|\mu_z|1>}{2\hbar\Omega}(-\Delta-\Omega)e^{\frac{-i\Omega t}{2}}\right] \\ C_1(t) &= \frac{\hbar e^{\frac{i\Delta t}{2}}}{2\Omega}\left[-\Delta e^{\frac{i\Omega t}{2}} + \Omega e^{\frac{i\Omega t}{2}} + \Delta e^{\frac{-i\Omega t}{2}} + \Omega e^{\frac{-i\Omega t}{2}}\right] \\ C_1(t) &= \frac{e^{\frac{i\Delta t}{2}}}{\Omega}\left[\Omega\left(\frac{e^{\frac{i\Omega t}{2}} + e^{\frac{-i\Omega t}{2}}}{2}\right) - i\Delta\left(\frac{e^{\frac{i\Omega t}{2}} - e^{\frac{-i\Omega t}{2}}}{2i}\right)\right] \\ C_1(t) &= \frac{e^{\frac{i\Delta t}{2}}}{\Omega}\left[\Omega cos\frac{\Omega t}{2} - i\Delta sin\frac{\Omega t}{2}\right] \end{aligned}$$

$$\boxed{C_1(t) = e^{\frac{i\Delta t}{2}}\left[cos\frac{\Omega t}{2} - \frac{i\Delta}{\Omega}sin\frac{\Omega t}{2}\right]} \tag{21.18}$$

Desired final expression for $C_1(t)$.

Now for $C_2(t)$

$$\begin{aligned} C_2(t) &= e^{\frac{-i\Delta t}{2}} \left[\frac{\epsilon_0 < 2|\mu_z|1 >}{2\hbar\Omega} e^{\frac{i\Omega t}{2}} - \frac{\epsilon_0 < 2|\mu_z|1 >}{2\hbar\Omega} e^{\frac{-i\Omega t}{2}} \right] \\ C_2(t) &= \frac{i\epsilon_0 < 2|\mu_z|1 >}{\hbar\Omega} e^{\frac{-i\Delta t}{2}} \left(\frac{e^{\frac{i\Omega t}{2}} - e^{\frac{-i\Omega t}{2}}}{2i} \right) \end{aligned}$$

$$\boxed{C_2(t) = \tfrac{i\epsilon_0 <2|\mu_z|1>}{\hbar\Omega} e^{\frac{-i\Delta t}{2}} sin\tfrac{\Omega t}{2}} \qquad (21.19)$$

Desired final expression for $C_2(t)$.

Summary

$$\begin{aligned} C_1(t) &= e^{\frac{i\Delta t}{2}} \left[cos\frac{\Omega t}{2} - \frac{i\Delta}{\Omega} sin\frac{\Omega t}{2} \right] \\ C_2(t) &= \frac{i\epsilon_0 < 2|\mu_z|1 >}{\hbar\Omega} e^{\frac{-i\Delta t}{2}} sin\frac{\Omega t}{2} \end{aligned}$$

Now one can calculate the coefficients at any time after the perturbation has been switched on.

Now let's derive P_1 and P_2 the probabilities of being in states 1 or 2 as a function of time. Recall that

$$\begin{aligned} P_1(t) &= |C_1(t)|^2 \\ P_2(t) &= |C_2(t)|^2 \end{aligned}$$

We get

$$\begin{aligned} P_1 &= cos^2\frac{\Omega t}{2} + \left(\frac{\Delta}{\Omega}\right)^2 sin^2\frac{\Omega t}{2} \\ &= cos^2\frac{\Omega t}{2} + \left(\frac{\Delta}{\Omega}\right)^2 [1 - cos^2\frac{\Omega t}{2}] \\ &= cos^2\frac{\Omega t}{2} + \left(\frac{\Delta}{\Omega}\right)^2 - (\frac{\Delta}{\Omega})^2 cos^2\frac{\Omega t}{2} \\ &= \left(\frac{\Delta}{\Omega}\right)^2 + \left[1 - \left(\frac{\Delta}{\Omega}\right)^2\right] cos^2\frac{\Omega t}{2} \\ &= \left(\frac{\Delta}{\Omega}\right)^2 + \left[\frac{\Omega^2 - \Delta^2}{\Omega^2}\right] cos^2\frac{\Omega t}{2} \end{aligned}$$

where recall that $\Delta^2 = (\omega - \omega_{21})^2$ and $\Omega^2 = \Delta^2 + \frac{\epsilon_0^2|<1|\mu_z|2>|^2}{\hbar^2}$ so that $\Omega^2 - \Delta^2 = \frac{\epsilon_0^2|<1|\mu_z|2>|^2}{\hbar^2}$. We get

$$\boxed{\left(\frac{\Delta}{\Omega}\right)^2 + \frac{\epsilon_0^2|<2|\mu_z|1>|^2}{\hbar^2\Omega^2} cos^2\frac{\Omega t}{2}} \tag{21.20}$$

$$\boxed{P_2 = \frac{\epsilon_0^2|<2|\mu_z|1>|^2}{\hbar^2\Omega^2} sin^2\frac{\Omega t}{2}} \tag{21.21}$$

These are the final expression for the probabilities of being in either states 1 or 2.

Note that $P_1 + P_2 = 1$ as expected.

Now finally to end this, at resonance ($\omega = \omega_{21}$), $\Delta = 0$ so that $\Omega^2 \to \frac{\epsilon_0^2|<1|\mu_z|2>|^2}{\hbar^2}$ or $\Omega \to \frac{\epsilon_0|<1|\mu_z|2>|}{\hbar}$. We get

$$\boxed{P_1 = cos^2\frac{\epsilon_0<1|\mu_z|2>t}{2\hbar}} \tag{21.22}$$

$$\boxed{P_2 = sin^2\frac{\epsilon_0<1|\mu_z|2>t}{2\hbar}} \tag{21.23}$$

so that the populations of states 1 and 2 oscillate in time.

You can see that when $\frac{\epsilon_0<1|\mu_z|2>t}{2\hbar} = \frac{\pi}{2}$, $P_1 = 0$ and $P_2 = 1$. Likewise when $\frac{\epsilon_0<1|\mu_z|2>t}{2\hbar} = \pi$ we get $P_1 = 1$ and $P_2 = 0$. This is where the terminology $\frac{\pi}{2}$ and π pulses comes from. You will often hear of such pulses in NMR terminology.

Finally, apart from demonstrating the Rabi oscillations and Rabi formulas, you can see that solving these differential equations gets tough pretty fast. This was a 2-level system. So as a consequence, people generally resort to time-dependent perturbation theory to solve things.

Chapter 22

Multilevel absorption, Schrodinger Representation

Ok, lets do this again. Practice makes perfect. This time do not assume a 2-level system.

Start with the electric field of light

$$\epsilon = \epsilon_0 cos\omega t$$

The interaction between the molecule's dipole moment and electric field is then

$$\begin{aligned} H^{(1)} &= -\mu \cdot \epsilon \\ &= -\mu \cdot \epsilon_0 cos\omega t \end{aligned}$$

Choose the z component for convenience.

$$\boxed{H_z^{(1)} = -\mu_z \epsilon_0 cos\omega t} \tag{22.1}$$

The Hamiltonian is then

$$H = H^{(0)} + H^{(1)}$$

or

$$\boxed{H = H^{(0)} - \mu_z cos\omega t} \tag{22.2}$$

The time dependent Schrodinger equation is

$$i\hbar \frac{d\Psi_n(r,t)}{dt} = H\Psi_n(r,t)$$

where a general expression of $\Psi_n(r,t)$ is a linear combination of zero order wavefunctions with time dependent coefficients.

$$\Psi(r,t) = \sum_n C_n(t)\Psi_n(r)e^{\frac{-i\epsilon_n^{(0)}t}{\hbar}}$$

$$\boxed{\Psi(r,t) = \sum_n C_n(t)\Psi_n(r,t)} \tag{22.3}$$

Replace the general wavefunction into the time dependent Schrodinger equation.

$$i\hbar\frac{d}{dt}\sum_n C_n(t)\Psi_n(r,t) = (H^{(0)} + H^{(1)})\sum_n C_n(t)\Psi_n(r,t)$$

$$\begin{aligned} & i\hbar\sum_n\left[C_n(t)\frac{d\Psi_n(r,t)}{dt} + \Psi_n(r,t)\frac{dC_n(t)}{dt}\right] \\ = \; & H^{(0)}\sum_n C_n(t)\Psi_n(r,t) + H^{(1)}\sum_n C_n(t)\Psi_n(r,t) \end{aligned}$$

The first two terms on either the right or left hand side will cancel since they are equivalent.

$$\begin{aligned} i\hbar C_n\frac{d\Psi_n(r,t)}{dt} &= H^{(0)}C_n\Psi_n(r,t) \\ i\hbar\frac{d\Psi_n(r,t)}{dt} &= H^{(0)}\Psi_n(r,t) \end{aligned}$$

So once these terms are dropped we are left with

$$i\hbar\sum_n \Psi_n(r,t)\frac{dC_n}{dt} = H^{(1)}\sum_n C_n(t)\Psi_n(r,t)$$

Now multiply/integrate both sides by $\Psi_k^{(0)}$

$$i\hbar\sum_n < k|n > e^{\frac{-i\epsilon_n^{(0)}t}{\hbar}}\frac{dC_n}{dt} = \sum_n C_n < k|H^{(1)}|n > e^{\frac{-i\epsilon_n^{(0)}t}{\hbar}}$$

on the left side you can see that $n = k$

$$i\hbar e^{\frac{-i\epsilon_k^{(0)}t}{\hbar}}\frac{dC_k}{dt} = \sum_n C_n < k|H^{(1)}|n > e^{\frac{-i\epsilon_n^{(0)}t}{\hbar}}$$

Multiply both sides by $e^{\frac{i\epsilon_k^{(0)}t}{\hbar}}$

$$i\hbar\frac{dC_k}{dt} = \sum_n C_n < k|H^{(1)}|n > e^{\frac{i(\epsilon_k^{(0)}-\epsilon_n^{(0)})t}{\hbar}}$$

where $\omega_{kn} = \frac{(\epsilon_k - \epsilon_n)}{\hbar}$ leaving

$$\boxed{i\hbar\frac{dC_k}{dt} = \sum_n C_n < k|H^{(1)}|n > e^{i\omega_{kn}t}} \tag{22.4}$$

This is our desired expression.

Now you have this expression for every state. To simplify, take a time dependent perturbation theory approach and assume an initial state m.

$$\begin{aligned} C_m(t) &\simeq 1 \\ C_{n\neq m}(t) &\simeq 0 \end{aligned}$$

$$i\hbar\frac{dC_k}{dt} = C_m(t) < k|H^{(1)}|m > e^{i\omega_{km}t}$$

$$\boxed{i\hbar\frac{dC_k}{dt} =< k|H^{(1)}|m > e^{i\omega_{km}t}} \tag{22.5}$$

Our perturbation theory approximation.

Now recall that $H^{(1)} = -\mu_z\epsilon_0 cos\omega t$.

$$\begin{aligned} i\hbar\frac{dC_k}{dt} &= < k| - \mu_z\epsilon_0 cos\omega t|m > e^{i\omega_{km}t} \\ i\hbar\frac{dC_k}{dt} &= -\epsilon_0 < k|\mu_z\left(\frac{e^{i\omega t} + e^{-i\omega t}}{2}\right)|m > e^{i\omega_{km}t} \\ i\hbar\frac{dC_k}{dt} &= -\frac{\epsilon_0}{2} < k|\mu_z|m > \left(e^{i(\omega+\omega_{km})t} + e^{-i(\omega-\omega_{km})t}\right) \end{aligned}$$

Solve for $C_k(t)$.

$$\frac{dC_k}{dt} = -\frac{\epsilon_0 < k|\mu_z|m >}{2i\hbar}\left(e^{i(\omega+\omega_{km})t} + e^{-i(\omega-\omega_{km})t}\right)$$

Inegrate this expression. Recall, however, that when you integrate $\frac{dC_k}{dt}$ you also get a constant of integration.

$$C_k(t) = C_k(t=0) - \frac{\epsilon_0 < k|\mu_z|m >}{2i\hbar}\int_0^t e^{i(\omega+\omega_{km})t'} + e^{-i(\omega-\omega_{km})t'}dt'$$

but $C_k(t=0) = \delta_{km}$ giving

$$C_k(t) = \delta_{km} - \frac{\epsilon_0 < k|\mu_z|m >}{2i\hbar} \int_0^t e^{i(\omega+\omega_{km})t'} + e^{-i(\omega-\omega_{km})t'} dt'$$

We get

$$\boxed{C_k^{(0)}(t) = \delta_{km}} \tag{22.6}$$

$$\boxed{C_k^{(1)}(t) = -\tfrac{\epsilon_0 < k|\mu_z|m >}{2i\hbar} \int_0^t e^{i(\omega+\omega_{km})t'} + e^{-i(\omega-\omega_{km})t'} dt'} \tag{22.7}$$

Focus on the first order term and integrate it.

$$\begin{aligned}
C_k^{(1)}(t) &= -\frac{\epsilon_0 < k|\mu_z|m >}{2i\hbar} \int_0^t e^{i(\omega+\omega_{km})t'} + e^{-i(\omega-\omega_{km})t'} dt' \\
&= -\frac{\epsilon_0 < k|\mu_z|m >}{2i\hbar} \left[\frac{(e^{i(\omega+\omega_{km})t} - 1)}{i(\omega+\omega_{km})} - \frac{(e^{-i(\omega-\omega_{km})t} - 1)}{i(\omega-\omega_{km})} \right] \\
&= \frac{\epsilon_0 < k|\mu_z|m >}{2\hbar} \left[\frac{(e^{\frac{i(\hbar\omega+\hbar\omega_k-\hbar\omega_m)t}{\hbar}} - 1)\hbar}{(\hbar\omega+\hbar\omega_k-\hbar\omega_m)} - \frac{(e^{\frac{-i(\hbar\omega-\hbar\omega_k+\hbar\omega_m)t}{\hbar}} - 1)\hbar}{(\hbar\omega-\hbar\omega_k+\hbar\omega_m)} \right] \\
&= \frac{\epsilon_0 < k|\mu_z|m >}{2} \left[\frac{(e^{\frac{i(h\nu+\epsilon_k-\epsilon_m)t}{\hbar}} - 1)}{(h\nu+\epsilon_k-\epsilon_m)} - \frac{(e^{\frac{-i(h\nu-\epsilon_k+\epsilon_m)t}{\hbar}} - 1)}{(h\nu-\epsilon_k+\epsilon_m)} \right]
\end{aligned}$$

$$\boxed{C_k^{(1)}(t) = \tfrac{\epsilon_0 < k|\mu_z|m >}{2} \left[\tfrac{(e^{\frac{i(\epsilon_k-\epsilon_m+h\nu)t}{\hbar}} - 1)}{(\epsilon_k-\epsilon_m+h\nu)} + \tfrac{(e^{\frac{i(\epsilon_k-\epsilon_m-h\nu)t}{\hbar}} - 1)}{(\epsilon_k-\epsilon_m-h\nu)} \right]} \tag{22.8}$$

The first term is the non-resonant or anti-resonant term. The second term is the resonant term.

When $h\nu = \epsilon_k - \epsilon_m$ the resonant term will dominate. We can drop the 1st term as an approximation. This is called the Rotating Wave approximation.

$$C_k^{(1)}(t) \simeq \frac{\epsilon_0 < k|\mu_z|m >}{2} \frac{(e^{\frac{i(\epsilon_k-\epsilon_m-h\nu)t}{\hbar}} - 1)}{(\epsilon_k - \epsilon_m - h\nu)}$$

Pull out $e^{\frac{i(\epsilon_k-\epsilon_m-h\nu)t}{2\hbar}}$ like before.

$$C_k^{(1)}(t) \simeq \frac{i\epsilon_0 < k|\mu_z|m >}{2i} e^{\frac{i(\epsilon_k^{(0)}-\epsilon_m^{(0)}-h\nu)t}{2\hbar}} \left(\frac{e^{\frac{i(\epsilon_k^{(0)}-\epsilon_m^{(0)}-h\nu)t}{2\hbar}} - e^{\frac{-i(\epsilon_k^{(0)}-\epsilon_m^{(0)}-h\nu)t}{2\hbar}}}{\epsilon_k - \epsilon_m - h\nu} \right)$$

$$\boxed{C_k^{(1)}(t) \simeq \frac{i\epsilon_0<k|\mu_z|m>}{(\epsilon_k-\epsilon_m-h\nu)} e^{\frac{i(\epsilon_k-\epsilon_m-h\nu)t}{2\hbar}} sin[\frac{(\epsilon_k-\epsilon_m-h\nu)t}{2\hbar}]} \tag{22.9}$$

This is our desired time dependent coefficient.

Now let's find the transition probability.

$$\begin{aligned} P_k &= |C_k(t)|^2 \\ &= \frac{\epsilon_0^2| < k|\mu_z|m > |^2}{(\epsilon_k - \epsilon_m - h\nu)^2} sin^2[\frac{(\epsilon_k - \epsilon_m - h\nu)t}{2\hbar}] \end{aligned}$$

$$\boxed{P_k = \epsilon_0^2| < k|\mu_z|m > |^2 \frac{sin^2\left[\frac{(\epsilon_k-\epsilon_m-h\nu)t}{2\hbar}\right]}{(\epsilon_k-\epsilon_m-h\nu)^2}} \tag{22.10}$$

This is our desired transition probability.

Some extra stuff now. For perfectly monochromatic light and when $h\nu = \epsilon_k - \epsilon_m$ what happens? To evaluate this apply L'Hopital's rule which states that if

$$\begin{aligned} lim_{x\to c} f(x) &= 0 \\ lim_{x\to c} g(x) &= 0 \end{aligned}$$

where in both cases c is finite, then

$$lim_{x\to c}\frac{f(x)}{g(x)} = lim_{x\to c}\frac{f^{'}(x)}{g^{'}(x)}$$

Recast P_k in terms of $x = (\epsilon_k - \epsilon_m - h\nu)$

$$\begin{aligned} P_k &= \epsilon_0^2| < k|\mu_z|m > |^2 \frac{sin^2\left[\frac{xt}{2\hbar}\right]}{x^2} \\ lim_{x\to 0} P_k &= \epsilon_0^2| < k|\mu_z|m > |^2 \frac{\left[2sin\frac{xt}{2\hbar}cos\frac{xt}{2\hbar}\frac{t}{2\hbar}\right]}{2x} \\ lim_{x\to 0} P_k &= \epsilon_0^2| < k|\mu_z|m > |^2 \frac{\left(\frac{t}{2\hbar}\right) sin\left(\frac{xt}{\hbar}\right)}{2x} \\ lim_{x\to 0} P_k &= \epsilon_0^2| < k|\mu_z|m > |^2 \left(\frac{t}{4\hbar}\right)\left(\frac{sin\left(\frac{xt}{\hbar}\right)}{x}\right) \end{aligned}$$

Use L'Hopital's rule again.

$$\begin{aligned}
lim_{x\rightarrow 0}P_k &= \epsilon_0^2| < k|\mu_z|m > |^2\left(\frac{t}{4\hbar}\right)\left[\frac{\left(\frac{t}{\hbar}\right)cos\left(\frac{xt}{\hbar}\right)}{1}\right] \\
lim_{x\rightarrow 0}P_k &= \epsilon_0^2| < k|\mu_z|m > |^2\left(\frac{t^2}{4\hbar^2}\right)\left[\frac{cos\left(\frac{xt}{\hbar}\right)}{1}\right] \\
lim_{x\rightarrow 0}P_k &= \epsilon_0^2| < k|\mu_z|m > |^2\left(\frac{t^2}{4\hbar^2}\right)\frac{lim_{x\rightarrow 0}cos\frac{xt}{\hbar}}{lim_{x\rightarrow 0}1} \\
lim_{x\rightarrow 0}P_k &= \epsilon_0^2| < k|\mu_z|m > |^2\left(\frac{t^2}{4\hbar^2}\right)
\end{aligned}$$

$$\boxed{lim_{x\rightarrow 0}P_k = \epsilon_0^2| < k|\mu_z|m > |^2\left(\frac{t^2}{4\hbar^2}\right)} \tag{22.11}$$

So in principle for perfectly monochromatic light exactly on resonance with the transition, the transition probability will increase quadratically with time.

Chapter 23

Rates, Schrodinger Representation

Since we have the probability of a given transition we desire the rate of the transitions. This is evaluated as the rate of change of the probability. Consider some examples provided below.

Sinusoidal perturbation, monochromatic light

In the case of a sinusoidal perturbation we derived the general transition probability of the form

$$\begin{aligned} P_k &= |C_k|^2 \\ &= \epsilon_0^2 | < k|\mu_z|m > |^2 \frac{sin^2\left[\frac{(\epsilon_k - \epsilon_m - h\nu)t}{2\hbar}\right]}{(\epsilon_k - \epsilon_m - h\nu)^2} \end{aligned}$$

Let's simplify and consolidate our notation by letting $(\epsilon_k - \epsilon_m) = h\nu_0$. We get

$$P_k = \epsilon_0^2 | < k|\mu_z|m > |^2 \frac{sin^2\left[\frac{(h\nu_0 - h\nu)t}{2\hbar}\right]}{(h\nu_0 - h\nu)^2}$$

Now convert to ω and ω_0 notation since $h\nu = \hbar\omega$.

$$P_k = \frac{\epsilon_0^2 | < k|\mu_z|m > |^2}{\hbar^2} \frac{sin^2\left[\frac{(\omega_0 - \omega)t}{2}\right]}{(\omega_0 - \omega)^2}$$

Now let $x = \left(\frac{\omega_0 - \omega}{2}\right)$ so that $(\omega_0 - \omega) = 2x$.

$$\begin{aligned} P_k &= \frac{\epsilon_0^2 | < k|\mu_z|m > |^2}{\hbar^2} \frac{sin^2(xt)}{4x^2} \\ &= \frac{\epsilon_0^2 | < k|\mu_z|m > |^2}{4\hbar^2} \frac{sin^2 xt}{x^2} \end{aligned}$$

Now the transition rate is $R = \frac{dP_k}{dt}$

$$\begin{aligned} R &= \frac{dP_k}{dt} \\ &= \frac{\epsilon_0^2 | < k|\mu_z|m > |^2}{4\hbar^2 x^2} 2sinxt(x)cosxt \\ &= \frac{\epsilon_0^2 | < k|\mu_z|m > |^2}{2\hbar^2 x} sinxtcosxt \\ &= \frac{\epsilon_0^2 | < k|\mu_z|m > |^2}{2\hbar^2 x} (\frac{1}{2} sin2xt) \\ &= \frac{\epsilon_0^2 | < k|\mu_z|m > |^2}{4\hbar^2} \frac{sin2xt}{x} \end{aligned}$$

Now replace $x = (\frac{\omega_0 - \omega}{2})$ into the above expression to get

$$\boxed{R = \frac{\epsilon_0^2 |<k|\mu_z|m>|^2}{2\hbar^2} \frac{sin[(\omega_0 - \omega)t]}{(\omega_0 - \omega)}} \tag{23.1}$$

Note that the transition rate will oscillate with time. It is not constant.

White light perturbation

Here we will expand on our perturbation theory result for monochromatic light and expand it to encompass the case where we have a spread of frequencies or in the extreme case, white light.

For simplicity, assume that we are dealing with a continuous (white) distribution of frequencies $\rho(\omega)$ is constant or "uniform".

Starting with the general time dependent perturbation theory expression for the transition probability of a sinusoidal monochromatic perturbation we have

$$\begin{aligned} P_k &= |C_k|^2 \\ &= \epsilon_0^2 | < k|\mu_z|m > |^2 \frac{sin^2[\frac{(\epsilon_k - \epsilon_m - h\nu)t}{2\hbar}]}{(\epsilon_k - \epsilon_m - h\nu)^2} \end{aligned}$$

Let's consolidate our notation again for convenience $\hbar\omega_0 = (\epsilon_k - \epsilon_m)$.

$$P_k = \frac{\epsilon_0^2| < k|\mu_z|m > |^2}{\hbar^2} \frac{sin^2[\frac{(\omega_0-\omega)t}{2}]}{(\omega_0-\omega)^2}$$

Now this expression, as noted, is only for one frequency. To get an equivalent expression for a spread of frequencies we must integrate over the entire distribution of ω.

$$P_{ktot} = \int_0^\infty \frac{\epsilon_0^2| < k|\mu_z|m > |^2}{\hbar^2} \frac{sin^2 \frac{\omega_0-\omega}{2} t}{(\omega_0-\omega)^2}\rho(\omega)d\omega$$

where $\rho(\omega)$ is the density of ω. But since $\rho(\omega)$ is constant call it ρ_0

$$P_{ktot} = \frac{\epsilon_0^2| < k|\mu_z|m > |^2}{\hbar^2}\rho_0 \int_0^\infty \frac{sin^2 \frac{\omega_0-\omega}{2} t}{(\omega_0-\omega)^2}d\omega$$

To further simplify things, let the bottom limit go to $-\infty$. (The integrand doesn't really contribute significanlty here anyway)

$$P_{ktot} = \frac{\epsilon_0^2| < k|\mu_z|m > |^2}{\hbar^2}\rho_0 \int_{-\infty}^\infty \frac{sin^2 \frac{\omega_0-\omega}{2} t}{(\omega_0-\omega)^2}d\omega$$

Let $x = (\frac{\omega_0-\omega}{2})t$ and $dx = -\frac{t}{2}d\omega$. Also remember to change the limits of integration.

$$\begin{aligned} P_{ktot} &= \frac{\epsilon_0^2| < k|\mu_z|m > |^2}{\hbar^2}\rho_0 \int_\infty^{-\infty} \frac{sin^2 x}{4x^2}\left(\frac{-2dx}{t}\right)t^2 \\ &= -\frac{\epsilon_0^2| < k|\mu_z|m > |^2}{2\hbar^2}\rho_0 t \int_\infty^{-\infty} \frac{sin^2 x}{x^2}dx \\ &= \frac{\epsilon_0^2\rho_0 t| < k|\mu_z|m > |^2}{2\hbar^2} \int_{-\infty}^{\infty} \frac{sin^2 x}{x^2}dx \end{aligned}$$

Look up the integral and find that $\int_{-\infty}^{\infty} \frac{sin^2 x}{x^2}dx = \pi$.

$$P_{ktot} = \frac{\epsilon_0^2\rho_0 t| < k|\mu_z|m > |^2\pi}{2\hbar^2}$$

$$\boxed{P_{ktot} = \frac{\epsilon_0^2\rho_0\pi|<k|\mu_z|m>|^2 t}{2\hbar^2}} \qquad (23.2)$$

Desired transition probability for white light excitation.

Now what is the transition rate?

$$\boxed{R = \frac{dP_{ktot}}{dt} = \frac{\epsilon_0^2 \rho_0 \pi |<k|\mu_z|m>|^2}{2\hbar^2}} \tag{23.3}$$

Note that this time the rate is constant, not oscillating with time. Also this is basically Fermi's Golden rule (actually his 2nd Golden Rule) when recast not as white light but as a spread over multiple final states.

Sinusoidal perturbation, monochromatic light, redux

Let's assume a 2-level system again. Assume also a sinusoidal perturbation and assume monochromatic light. Derive the transition probability from state 2 to state 1. (Recall that in the first example we did the transition from state 1 to state 2. This is just the reverse.) Assume that $\epsilon_2 > \epsilon_1$.

Start with the form of the perturbation

$$\begin{aligned} \epsilon &= \epsilon_0 cos\omega t \\ H^{(1)} &= -\mu \cdot \epsilon = -\mu \cdot \epsilon_0 cos\omega t \end{aligned}$$

For simplicity take the z component leaving

$$H^{(1)} = -\mu_z \epsilon_0 cos\omega t$$

The form of the wavefunction is a linear combination of zero order wavefunctions with time dependent coefficients.

$$\Psi(r,t) = \sum_n C_n(t)\Psi_n(r,t)$$

Since we only have two levels

$$\Psi(r,t) = C_1(t)\Psi_1(r,t) + C_2(t)\Psi_2(r,t)$$

where

$$\begin{aligned} \Psi_1(r,t) &= \Psi_1(r)e^{\frac{-i\epsilon_1 t}{\hbar}} \\ \Psi_2(r,t) &= \Psi_2(r)e^{\frac{-i\epsilon_2 t}{\hbar}} \end{aligned}$$

The time dependent Schrodinger equation is

$$i\hbar\frac{d\Psi(r,t)}{dt} = H\Psi(r,t)$$

where $H = H^{(0)} + H^{(1)}(t)$. We then have

$$\begin{aligned} i\hbar\frac{d}{dt}\Psi(r,t) &= (H^{(0)} + H^{(1)})\Psi(r,t) \\ i\hbar\frac{d}{dt}[C_1\Psi_1 + C_2\Psi_2] &= (H^{(0)} + H^{(1)})[C_1\Psi_1 + C_2\Psi_2] \end{aligned}$$

where the time dependences of C_1, C_2, Ψ_1, Ψ_2 are understood. Expanding we get

$$\begin{aligned} & i\hbar C_1\frac{d\Psi_1}{dt} + i\hbar C_2\frac{d\Psi_2}{dt} + i\hbar\Psi_1\frac{dC_1}{dt} + i\hbar\Psi_2\frac{dC_2}{dt} \\ = \;& C_1H^{(0)}\Psi_1 + C_2H^{(0)}\Psi_2 + C_1H^{(1)}\Psi_1 + C_2H^{(1)}\Psi_2 \end{aligned}$$

from before we know that the first two terms on either the left or right hand side are equivalent and will dissapear leaving

$$i\hbar\Psi_1\frac{dC_1}{dt} + i\hbar\Psi_2\frac{dC_2}{dt} = C_1H^{(1)}\Psi_1 + C_2H^{(1)}\Psi_2$$

where recall that

$$\begin{aligned} \Psi_1 &= \Psi_1(r)e^{\frac{-i\epsilon_1 t}{\hbar}} \\ \Psi_2 &= \Psi_2(r)e^{\frac{-i\epsilon_2 t}{\hbar}} \end{aligned}$$

The equation then becomes

$$i\hbar\Psi_1\frac{dC_1}{dt}e^{\frac{-i\epsilon_1 t}{\hbar}} + i\hbar\Psi_2\frac{dC_2}{dt}e^{\frac{-i\epsilon_2 t}{\hbar}} = C_1H^{(1)}\Psi_1e^{\frac{-i\epsilon_1 t}{\hbar}} + C_2H^{(1)}\Psi_2e^{\frac{-i\epsilon_2 t}{\hbar}}$$

Now recall that we want to know more about $C_1(t)$ so multiply/integrate both sides by $\Psi_1^{(0)*}$.

$$\begin{aligned} & i\hbar <1|1> \frac{dC_1}{dt}e^{\frac{-i\epsilon_1^{(0)} t}{\hbar}} + i\hbar <1|2> \frac{dC_2}{dt}e^{\frac{-i\epsilon_2^{(0)} t}{\hbar}} \\ = \;& C_1 <1|H^{(1)}|1> e^{\frac{-i\epsilon_1^{(0)} t}{\hbar}} + C_2 <1|H^{(1)}|2> e^{\frac{-i\epsilon_2^{(0)} t}{\hbar}} \end{aligned}$$

Use the normalization and orthogonality relations between states 1 and 2 to simplify. This leaves

$$i\hbar\frac{dC_1}{dt}e^{\frac{-i\epsilon_1^{(0)} t}{\hbar}} = C_1 <1|H^{(1)}|1> e^{\frac{-i\epsilon_1^{(0)} t}{\hbar}} + C_2 <1|H^{(1)}|2> e^{\frac{-i\epsilon_2^{(0)} t}{\hbar}}$$

Multiply both sides by $e^{\frac{i\epsilon_1^{(0)}t}{\hbar}}$ to get

$$i\hbar\frac{dC_1}{dt} = C_1 < 1|H^{(1)}|1> +C_2 < 1|H^{(1)}|2> e^{\frac{-i(\epsilon_2^{(0)}-\epsilon_1^{(0)})t}{\hbar}}$$

Let $\omega_{21} = \frac{(\epsilon_2-\epsilon_1)}{\hbar}$

$$\boxed{i\hbar\frac{dC_1}{dt} = C_1 < 1|H^{(1)}|1> +C_2 < 1|H^{(1)}|2> e^{-i\omega_{21}t}} \tag{23.4}$$

Now invoke a time dependent perturbation theory approximation and say

$$\begin{aligned} C_2(t) &\simeq 1 \\ C_1(t) &\simeq 0 \end{aligned}$$

This gives

$$\boxed{i\hbar\frac{dC_1}{dt} =< 1|H^{(1)}|2> e^{-i\omega_{21}t}} \tag{23.5}$$

Now recall that $H^{(1)} = -\mu_z\epsilon_0 cos\omega t$

$$\begin{aligned} i\hbar\frac{dC_1}{dt} &= < 1| - \mu_z\epsilon_0 cos\omega t|2> e^{-i\omega_{21}t} \\ &= -\epsilon_0 < 1|\mu_z|2> cos\omega t e^{-i\omega_{21}t} \\ &= -\epsilon_0 < 1|\mu_z|2> \frac{(e^{i\omega t}+e^{-i\omega t})}{2} e^{-i\omega_{21}t} \\ &= -\frac{\epsilon}{2} < 1|\mu_z|2> (e^{i(\omega-\omega_{21})t} + e^{-i(\omega+\omega_{21})t}) \end{aligned}$$

Ok so we have to integrate this approximation.

$$\frac{dC_1}{dt} = -\frac{\epsilon_0 < 1|\mu_z|2>}{2i\hbar}\left(e^{i(\omega-\omega_{21})t} + e^{-i(\omega+\omega_{21})t}\right)$$

Note that when you integrate $\frac{dC_1}{dt}$ you also get a constant of integration

$$C_1(t) = C_1(t=0) - \frac{\epsilon_0 < 1|\mu_z|2>}{2i\hbar}\int_0^t e^{i(\omega-\omega_{21})t'} + e^{-i(\omega+\omega_{21})t'}dt'$$

but $C_1(t=0) = \delta_{12}$

$$C_1(t) = \delta_{12} - \frac{\epsilon_0 < 1|\mu_z|2>}{2i\hbar}\int_0^t e^{i(\omega-\omega_{21})t'} + e^{-i(\omega+\omega_{21})t'}dt'$$

So we have

$$\begin{aligned} C_1^{(0)}(t) &= \delta_{12} \\ C_1^{(1)}(t) &= -\frac{\epsilon_0 < 1|\mu_z|2 >}{2i\hbar}\int_0^t e^{i(\omega-\omega_{21})t'} + e^{-i(\omega+\omega_{21})t'}dt' \end{aligned}$$

of which we will work with the first order correction $C_1^{(1)}(t)$.

Ok, let's continue

$$\begin{aligned} C_1^{(1)}(t) &= \int_0^t -\frac{\epsilon_0 < 1|\mu_z|2 >}{2i\hbar}\left(i(\omega-\omega_{21})t' + e^{-i(\omega+\omega_{21})t'}\right)dt' \\ &= -\frac{\epsilon_0 < 1|\mu_z|2 >}{2i\hbar}\int_0^t e^{i(\omega-\omega_{21})t'} + e^{-i(\omega+\omega_{21})t'}dt' \\ &= -\frac{\epsilon_0 < 1|\mu_z|2 >}{2i\hbar}\left[\frac{(e^{i(\omega-\omega_{21})t}-1)}{i(\omega-\omega_{21})} - \frac{(e^{-i(\omega+\omega_{21})t}-1)}{i(\omega+\omega_{21})}\right] \\ &= \frac{\epsilon_0 < 1|\mu_z|2 >}{2i\hbar}\left[-\frac{(e^{-i(\omega_{21}-\omega)t}-1)}{i(\omega_{21}-\omega)} + \frac{(e^{-i(\omega_{21}+\omega)t}-1)}{i(\omega_{21}+\omega)}\right] \\ &= \frac{\epsilon_0 < 1|\mu_z|2 >}{2\hbar}\left[\frac{(e^{-i(\omega_{21}-\omega)t}-1)}{(\omega_{21}-\omega)} - \frac{(e^{-i(\omega_{21}+\omega)t}-1)}{(\omega_{21}+\omega)}\right] \end{aligned}$$

At resonance the 1st term will dominate. Therefore we can drop the second term. This is called the Rotating Wave approximation.

$$C_1(t) = -\frac{\epsilon_0 < 1|\mu_z|2 >}{2\hbar}\frac{(e^{-i(\omega_{21}-\omega)t}-1)}{(\omega_{21}-\omega)}$$

Divide out $e^{\frac{-i(\omega_{21}-\omega)t}{2}}$

$$C_1(t) = -\frac{i\epsilon_0 < 1|\mu_z|2 >}{\hbar}\frac{e^{\frac{-i(\omega_{21}-\omega)t}{2}}}{(\omega_{21}-\omega)}\left[\frac{e^{\frac{-i(\omega_{21}-\omega)t}{2}} - e^{\frac{i(\omega_{21}-\omega)t}{2}}}{2i}\right]$$

$$\boxed{C_1(t) = \frac{i\epsilon_0 < 1|\mu_z|2 >}{\hbar}e^{\frac{-i(\omega_{21}-\omega)t}{2}}\frac{sin\left(\frac{\omega_{21}-\omega}{2}\right)t}{(\omega_{21}-\omega)}} \tag{23.6}$$

This is our desired expression for $C_1(t)$.

Now for the transition probability.

$$\begin{aligned} P_1 &= |C_1(t)|^2 \\ &= \frac{\epsilon_0^2| < 1|\mu_z|2 > |^2}{\hbar^2}\frac{sin^2\left(\frac{\omega_{21}-\omega}{2}\right)t}{(\omega_{21}-\omega)^2} \end{aligned}$$

$$\boxed{P_1 = \frac{\epsilon_0^2 |<1|\mu_z|2>|^2}{\hbar^2} \frac{sin^2\left(\frac{\omega_{21}-\omega}{2}\right)t}{(\omega_{21}-\omega)^2}} \tag{23.7}$$

Note that this is the same probability in the reverse case which we derived earlier.

$$\boxed{P_2 = \frac{\epsilon_0^2 |<2|\mu_z|1>|^2}{\hbar^2} \frac{sin^2\left(\frac{\omega_{21}-\omega}{2}\right)t}{(\omega_{21}-\omega)^2}} \tag{23.8}$$

The probability of stimulated emission is exactly the same as the probability of absorption for this case of a harmonic and monochromatic perturbation.

This is basically the equivalence of the Einstein B coefficients which we will discuss later. Note also that this and its counterpart problem say nothing about spontaneous emission (described by the Einstein A coefficient described later).

Chapter 24

2nd order time dependent perturbation theory

2nd order time dependent perturbation theory and Schrödinger/Interaction pictures

Suppose we want expressions for higher order time dependent perturbation theory. Recall that I said that you simply take the 1st order solution and plug it back into a system of coupled differential equations (our matrix if you will).

$$C_k^{(1)}(t) = \frac{1}{i\hbar}\int_0^t \langle k|H^{(1)}|n\rangle e^{i\omega_{kn}t'}dt' \qquad \text{1st order solution}$$

This expression above was for initial state n and final state k. Let's just rename the labels to prevent confusion. Call our initial state m and our final state n. So $k \to n$ and $n \to m$.

$$C_k^{(1)}(t) \to C_n^{(1)}(t) = \frac{1}{i\hbar}\int_0^t \langle n|H^{(1)}|m\rangle e^{i\omega_{nm}t'}dt' \tag{24.1}$$

Now feed this expression into the right hand side of our original coupled differential equation expression

$$i\hbar\frac{dC_k}{dt} = \sum_n C_n \langle k|H^{(1)}|n\rangle e^{i\omega_{kn}t}$$

So rather than assume $C_m(t) \simeq 1$ and $C_n(t) \simeq 0$ etc. (1st order time dependent perturbation theory) we feed it in the 1st order solution:

$$i\hbar\frac{dC_k}{dt} = \sum_n \langle k|H^{(1)}|n\rangle e^{i\omega_{kn}t}\left(\frac{1}{i\hbar}\right)\int_0^t \langle n|H^{(1)}|m\rangle e^{i\omega_{nm}t'}dt'$$

$$i\hbar\frac{dC_k^{(2)}}{dt} = \frac{1}{i\hbar}\sum_n \langle k|H^{(1)}|n\rangle e^{i\omega_{kn}t}\int_0^t \langle n|H^{(1)}|m\rangle e^{i\omega_{nm}t'}dt'$$

$$\frac{dC_k^{(2)}}{dt} = -\frac{1}{\hbar^2}\sum_n \langle k|H^{(1)}|n\rangle e^{i\omega_{kn}t}\int_0^t \langle n|H^{(1)}|m\rangle e^{i\omega_{nm}t'}dt'$$

Now integrate this expression to get $C_k^{(2)}(t)$

$$\boxed{C_k^{(2)}(t) = -\tfrac{1}{\hbar^2}\textstyle\sum_n \int_0^t dt'\langle k|H^{(1)}|n\rangle e^{i\omega_{kn}t'}\int_0^{t''}\langle n|H^{(1)}|m\rangle e^{i\omega_{nm}t''}dt''} \qquad (24.2)$$

This is our desired second order contribution. Recall that k is our final state, m is our initial state and n interestingly turns out to be an intermediate state. So even if the matrix element in 1st order time dependent perturbation theory $\langle k|H^{(1)}|m\rangle$ directly linking the initial and final states is 0 thus we can get a transition between m and k indirectly through an intermediate state.

Extension to higher order time dependent perturbation theory. Ok – so it's possible to go to higher orders but typically what happens is that people switch from the Schrödinger representation which we have been working in to what is called the interaction representation.

We will describe these "pictures" of quantum mechanics shortly but for now let's just go through the motions and see what the expressions look like.

First recall that exponentials have a corresponding Taylor series approximation

$$e^x = \frac{1}{0!} + \frac{x}{1!} + \frac{x^2}{2!} + \frac{x^3}{3!} + \cdots = \sum_l \frac{x^l}{l!}$$

Therefore,

$$
\begin{aligned}
e^{-\frac{iH_0t}{\hbar}}|n\rangle &= \sum_{l=0} \frac{(-\frac{iH_0t}{\hbar})^l}{l!}|n\rangle \\
&= \left(1 - \frac{iH_0t}{\hbar} + \dots\right)|n\rangle \\
&= |n\rangle - \frac{iH_0t}{\hbar}|n\rangle + \dots \\
&= |n\rangle - \frac{i\epsilon_0t}{\hbar}|n\rangle + \dots \qquad \text{(since } H_0|n\rangle = \epsilon_0|n\rangle\text{)} \\
&= \left(1 - \frac{i\epsilon_0t}{\hbar} + \dots\right)|n\rangle \\
&= e^{-\frac{i\epsilon_0t}{\hbar}}|n\rangle
\end{aligned}
$$

So our desired equivalence which we will need is that

$$\boxed{e^{-\frac{iH_0t}{\hbar}}|n\rangle = e^{-\frac{i\epsilon_0t}{\hbar}}|n\rangle} \tag{24.3}$$

Now note that

$$
\begin{aligned}
\langle k|H^{(1)}|n\rangle e^{i\omega_{kn}t} &= \langle k|H^{(1)}|n\rangle e^{\frac{i\left(\epsilon_k^{(0)}-\epsilon_n^{(0)}\right)t}{\hbar}} \\
&= e^{\frac{i\epsilon_k^{(0)}t}{\hbar}}\langle k|H^{(1)}|n\rangle e^{-\frac{i\epsilon_n^{(0)}t}{\hbar}} \\
&= \langle k|e^{\frac{i\epsilon_k^{(0)}t}{\hbar}}H^{(1)}e^{-\frac{i\epsilon_n^{(0)}t}{\hbar}}|n\rangle \\
&= \langle k|e^{\frac{iH_0t}{\hbar}}H^{(1)}e^{-\frac{iH_0t}{\hbar}}|n\rangle
\end{aligned}
$$

using our equivalence above.
Now define

$$\boxed{\langle k|H^{(1)'}|n\rangle = \langle k|e^{\frac{iH_0t}{\hbar}}H^{(1)}e^{-\frac{iH_0t}{\hbar}}|n\rangle} \tag{24.4}$$

or alternatively

$$\langle k|H^{(1)}|n\rangle_I = \langle k|e^{\frac{iH_0t}{\hbar}}H^{(1)}e^{-\frac{iH_0t}{\hbar}}|n\rangle$$

"I" for interaction.

$$V_{knI} = V_{kn}$$

but remember that it is $H^{(1)}$ that is getting changed.

Now reintroduce this notation into our previously derived expression for $C_k^{(2)}$ (2nd order time dependent perturbation theory) contribution.

$$\begin{aligned}
C_k^{(2)}(t) &= -\frac{1}{\hbar^2}\sum_n \int_0^t dt' \langle k|H^{(1)}|n\rangle e^{i\omega_{kn}t'} \int_0^{t'} dt'' \langle n|H^{(1)}|m\rangle e^{i\omega_{nm}t''} \\
&= -\frac{1}{\hbar^2}\sum_n \int_0^t dt' \int_0^{t'} dt'' \langle k|H^{(1)'}(t')|n\rangle\langle n|H^{(1)'}(t'')|m\rangle \\
&= -\frac{1}{\hbar^2}\langle k|\left[\sum_n \int_0^t dt' \int_0^{t'} dt'' H^{(1)'}(t')|n\rangle\langle n|H^{(1)'}(t'')|m\rangle\right] \\
&= \langle k|\left[-\frac{1}{\hbar^2}\int_0^t dt' \int_0^{t'} dt'' H^{(1)'}(t')\sum_n |n\rangle\langle n|H^{(1)'}(t'')\right]|m\rangle
\end{aligned}$$

But $\sum_n |n\rangle\langle n| = 1$ from the completeness theorem (or closure relation),

$$\boxed{C_k^{(2)}(t) = \langle k|\left[-\tfrac{1}{\hbar^2}\int_0^t dt' \int_0^{t'} dt'' H^{(1)'}(t')H^{(1)'}(t'')\right]|m\rangle} \tag{24.5}$$

Now generalizing this to get the nth order contribution

$$\boxed{C_k^{(3)}(t) = \langle k|\left[\tfrac{1}{(i\hbar)^3}\int_0^t dt' \int_0^{t'} dt'' \int_0^{t''} dt''' H^{(1)'}(t')H^{(1)'}(t'')H^{(1)'}(t''')\right]|m\rangle} \tag{24.6}$$

for the 3rd order contribution and

$$\boxed{C_k^{(4)}(t) = \langle k|\left[\tfrac{1}{(i\hbar)^4}\int_0^t dt' \int_0^{t'} dt'' \int_0^{t''} dt''' \int_0^{t'''} dt'''' H^{(1)'}(t')H^{(1)'}(t'')H^{(1)'}(t''')H^{(1)'}(t'''')\right]|m\rangle} \tag{24.7}$$

for the 4th order contribution, and so on for higher order contributions.

The whole thing can be put together as

$$C_k(t) = C_k^{(0)}(t) + C_k^{(1)}(t) + C_k^{(2)}(t) + \ldots$$

or

$$\begin{aligned}C_k(t) = \langle k| \Bigg[1 + \frac{1}{i\hbar}\int_0^t dt' H^{(1)'}(t') + \frac{1}{(i\hbar)^2}\int_0^t dt' \int_0^{t'} dt'' H^{(1)'}(t') H^{(1)'}(t'') + \\ \frac{1}{(i\hbar)^3}\int_0^t dt' \int_0^{t'} dt'' \int_0^{t''} dt''' H^{(1)'}(t') H^{(1)'}(t'') H^{(1)'}(t''') + \ldots \Bigg] |m\rangle \\ = \langle k| U(t) |m\rangle\end{aligned} \tag{24.8}$$

where

$$\begin{aligned}U(t) =& 1 + \frac{1}{i\hbar}\int_0^t dt' H^{(1)'}(t') + \frac{1}{(i\hbar)^2}\int_0^t dt' \int_0^{t'} dt'' H^{(1)'}(t') H^{(1)'}(t'') + \\ & \frac{1}{(i\hbar)^3}\int_0^t dt' \int_0^{t'} dt'' \int_0^{t''} dt''' H^{(1)'}(t') H^{(1)'}(t'') H^{(1)'}(t''') + \ldots\end{aligned} \tag{24.9}$$

is called the Dyson series

Chapter 25

Three pictures of quantum mechanics

The three pictures we are referring to are called the Schrodinger, Heisenberg and Interaction Representations.

You saw that in the previous section that we dealt with fairly long expressions for the 2nd order contribution $C_k^{(2)}$ in time dependent perturbation theory. It gets even longer in 3rd order and higher. We also saw that things could be simplified if we took the $e^{i\omega_{kn}t}$ terms in the integrals and split them into two and eventually pulled these exponentials into $< k|H^{(1)}|n >$ leading to $< k|H^{(1)'}|n >$ or $H^{(1)} \to H^{(1)'}$. This switch is more than just a convenience. It basically represents transitioning from one representation of quantum mechanics into another.

There are three standard representations or picture of quantum mechanics. They are called the Schrodinger, the Hiesenberg and Interaction representations. By default we have been working in the Schrodinger representation all this time.

Schrodinger Representation

In the Schrodinger Representation

- state vectors (or wavefunctions if you will) have time dependence
- operators are time independent

Start with the standard time dependent Schrodinger equation.

$$i\hbar\frac{d}{dt}|\Psi(t) >_s = H|\Psi(t) >_s$$

If the Hamiltonian, H, does not depend explicitly on time we can immediately integrate this to get

$$\begin{aligned} \frac{d|\Psi(t)>_s}{|\Psi(t)>_s} &= \frac{H}{i\hbar}dt = \frac{-iH}{\hbar}dt \\ ln|\Psi(t)>_s &= -\frac{iHt}{\hbar} + const \\ |\Psi(t)>_s &= e^{\frac{-iHt}{\hbar}}(const) \end{aligned}$$

where $(const) = |\Psi(t_0)>_s$. We get

$$\boxed{|\Psi(t)>_s = e^{\frac{-iHt}{\hbar}}|\Psi(t_0)>} \tag{25.1}$$

Here

$$\boxed{U(t) = e^{\frac{-iHt}{\hbar}}} \tag{25.2}$$

and is referred to as the time evolution operator. So you can see that in the Schrodinger representation state vectors evolve in time.

Now the generic operator A_s is time independent in the Schrodinger Representation. It's expectation value $< A >$ however evolves in time as dictated by the time dependence of $|\Psi(t)>_s$

$$\begin{aligned} < A(t) > &= < \Psi(t)_s|A_s|\Psi(t)_s > \\ &= < \Psi_s(t_0)|e^{\frac{iHt}{\hbar}}A_s e^{\frac{-iHt}{\hbar}}|\Psi_s(t_0) > \end{aligned}$$

Heisenberg Representation

In the Heisenberg Representation

- State vectors or wavefunctions are time independent
- Operators however are time dependent

So we have $|\Psi_H(t)>$ time independent. At $t = 0$

$$\boxed{|\Psi_h(t_0)> = |\Psi_s(t_0)>} \tag{25.3}$$

The Schrodinger and Heisenberg state vectors are equivalent at $t = 0$.

More generally though, the Heisenber state vector is defined by

$$\boxed{|\Psi_h(t)> = e^{\frac{iHt}{\hbar}}|\Psi_s(t)>} \tag{25.4}$$

but you recall that

$$|\Psi_s(t)>= e^{\frac{-iHt}{\hbar}}|\Psi_s(t_0)>$$

so that

$$|\Psi_h(t)>= e^{\frac{iHt}{\hbar}}e^{\frac{-iHt}{\hbar}}|\Psi_s(t_0)>= |\Psi_s(t_0)>$$

We are then left with

$$\boxed{|\Psi_h(t)>= |\Psi_s(t_0)>} \tag{25.5}$$

showing the time independence of the Heisenberg state vector.

Regarding operators, since expectation values are invariant to the change of representation for a generic operator A

$$\begin{aligned}<A> &= <\Psi_s(t)|A_s|\Psi_s(t)> \\ &= <\Psi_s(t_0)|e^{\frac{iHt}{\hbar}}A_s e^{\frac{-iHt}{\hbar}}|\Psi_s(t_0)> \\ &= <\Psi_s(t_0)|A_h|\Psi_s(t_0)>\end{aligned}$$

$$\boxed{<A>=<\Psi_h(t_0)|A_h|\Psi_h(t_0)>} \tag{25.6}$$

since $|\Psi_h(t_0)>= |\Psi_s(t_0)>$. Furthermore

$$\boxed{A_h = e^{\frac{iHt}{\hbar}}A_s e^{\frac{-iHt}{\hbar}}} \tag{25.7}$$

and you can see that this definition of the Heisenberg operator will evolve with time.

Interaction Representation

This representation is used when the Hamiltonian has a time dependent component. It is an intermediate picture between the Schrodinger and Heisenberg representations in that both the state vectors and operators will evolve with time. However their time developments are governed by different parts of the total Hamiltonian $H = H^{(0)} + H^{(1)}(t)$.

The evolution of the operator is dictated by the time independent component $H^{(0)}$. The evolution of the state vector is dictated by $H^{(1)}(t)$ the time dependent component.

Thus the interaction picture is intermediate between the Schrodinger picture in which only the state vectors change in time and the Heisenberg picture where only the operators are subject to time development.

Chapter 26

The interaction representation

The time dependent Schrodinger equation is

$$i\hbar\frac{d}{dt}|\Psi_s(t)>= H|\Psi_s(t)>$$

where we have explicitly used "s" to denote that we are working in the Schrodinger representation. Here

$$H = H^{(0)} + H^{(1)}$$

where $H^{(0)}$ is time independent and $H^{(1)}$ may or may not have time dependence. In the case we are concerned with $H^{(1)}$ is a function of time $H^{(1)}(t)$.

To derive results of the Schrodinger representation we define our interaction representation state vector as

$$\boxed{|\Psi_I(t)>= e^{\frac{iH^{(0)}t}{\hbar}}|\Psi_s(t)>} \tag{26.1}$$

and also note that at $t = 0$ the wavefunction is equivalent to the Heisenberg representation wavefunction. To better see this, recall that $|\Psi_s(t)>= e^{\frac{-iHt}{\hbar}}|\Psi_s(t_o)>$. But $H = H^{(0)} + H^{(1)}(t)$ so that $|\Psi_I(t)>\propto e^{\frac{-iH^{(1)}(t)}{\hbar}}$. You see tat it will behave in time as $H^{(1)}$.

We want to re-express our Schrodinger representation in the interaction representation so

$$|\Psi_s(t)>= e^{\frac{-iH^{(0)}t}{\hbar}}|\Psi_I(t)>$$

and plug this into the above Schrodinger equation.

$$i\hbar\frac{d}{dt}\left[e^{\frac{-iH^{(0)}t}{\hbar}}|\Psi_I(t)>\right] = (H^{(0)} + H^{(1)})\left[e^{\frac{-iH^{(0)}t}{\hbar}}|\Psi_I(t)>\right]$$

Use the chain rule to evaluate the derivative.

$$\begin{aligned} & i\hbar[e^{\frac{-iH^{(0)}t}{\hbar}}\frac{d|\Psi_I(t)>}{dt} - \frac{iH^{(0)}}{\hbar}e^{\frac{-iH^{(0)}t}{\hbar}}|\Psi_I(t)>] \\ = & (H^{(0)} + H^{(1)})[e^{\frac{-iH^{(0)}t}{\hbar}}|\Psi_I(t)>] \\ & i\hbar e^{\frac{-iH^{(0)}t}{\hbar}}\frac{d|\Psi_I(t)>}{dt} + H^{(0)}e^{\frac{-iH^{(0)}t}{\hbar}}|\Psi_I(t)> \\ = & H^{(0)}e^{\frac{-iH^{(0)}t}{\hbar}}|\Psi_I(t)> + H^{(1)}e^{\frac{-iH^{(0)}t}{\hbar}}|\Psi_I(t)> \end{aligned}$$

Cancel the common terms leaving

$$i\hbar e^{\frac{-iH^{(0)}t}{\hbar}}\frac{d|\Psi_I(t)>}{dt} = H^{(1)}e^{\frac{-iH^{(0)}t}{\hbar}}|\Psi_I(t)>$$

Now multiply both sides by $e^{\frac{iH^{(0)}t}{\hbar}}$. Recall however that since we are dealing with operators we must be careful with the order of operation. It must be preserved.

$$\begin{aligned} i\hbar e^{\frac{iH^{(0)}t}{\hbar}}e^{\frac{-iH^{(0)}t}{\hbar}}\frac{d|\Psi_I(t)>}{dt} &= e^{\frac{iH^{(0)}t}{\hbar}}H^{(1)}e^{\frac{-iH^{(0)}t}{\hbar}}|\Psi_I(t)> \\ i\hbar\frac{d|\Psi_I(t)>}{dt} &= \left(e^{\frac{iH^{(0)}t}{\hbar}}H^{(1)}e^{\frac{-iH^{(0)}t}{\hbar}}\right)|\Psi_I(t)> \end{aligned}$$

or let

$$\boxed{H^{(1)'} = e^{\frac{iH^{(0)}t}{\hbar}}H^{(1)}e^{\frac{-iH^{(0)}t}{\hbar}}} \tag{26.2}$$

Basically the operator $H^{(1)}$ recast in the new interaction representation. We have in summary

$$\boxed{i\hbar\frac{d|\Psi_I(t)>}{dt} = H^{(1)'}|\Psi_I(t)>} \tag{26.3}$$

So this expression is the Schrodinger equation in the interaction representation. Note that both operator and wavefunction have both been flipped over.

Now we simply integrate this expression to get the behavior of the system after the perturbation has been turned on.

$$\begin{aligned}
\frac{d|\Psi_I(t)>}{dt} &= \frac{1}{i\hbar}H^{(1)'}|\Psi_I(t)> \\
\int_{t_0}^{t}\frac{d|\Psi_I(t^{'})>}{dt^{'}}dt^{'} &= \frac{1}{i\hbar}\int_{t_0}^{t}H^{(1)'}|\Psi_I(t^{'})>dt^{'} \\
|\Psi_I(t)> -|\Psi_I(t_0)> &= \frac{1}{i\hbar}\int_{t_0}^{t}H^{(1)'}|\Psi_I(t^{'})>dt^{'}
\end{aligned}$$

$$\boxed{|\Psi_I(t)>=|\Psi_I(t_0)>+\tfrac{1}{i\hbar}\textstyle\int_{t_0}^{t}H^{(1)'}|\Psi_I(t^{'})>dt^{'}} \tag{26.4}$$

So you can see that this is our wavefunction with both zeroth and 1st order corrections as desired through the interaction representation. Now from this we develop our solution $|\Psi_I(t)>$ in powers of $H^{(1)'}$ by repetitive iteration. Basically take $|\Psi_I(t)>=|\Psi_I(t_0)>+\frac{1}{i\hbar}\int_{t_0}^{t}dt^{'}H^{(1)'}|\Psi_I(t^{'})>$ and feed it into itself (like a dog chasing its tail).

$$|\Psi_I(t)>=|\Psi_I(t_0)>+\frac{1}{i\hbar}\int_{t_0}^{t}dt^{'}H^{(1)'}|\Psi_I(t^{'})>$$

Iteration 1

$$\begin{aligned}
|\Psi_I(t)> &= |\Psi_I(t_0)>+\frac{1}{i\hbar}\int_{t_0}^{t}dt^{'}H^{(1)'}\left[|\Psi_I(t_0)>+\frac{1}{i\hbar}\int_{t_0}^{t}dt^{'}H^{(1)'}|\Psi_I(t^{'})>\right] \\
&= |\Psi_I(t_0)>+\frac{1}{i\hbar}\int_{t_0}^{t}dt^{'}H^{(1)'}|\Psi_I(t_0)>+\frac{1}{(i\hbar)^2}\int_{t_0}^{t}dt^{'}H^{(1)'}(t^{'})\int_{t_0}^{t^{'}}dt^{''}H^{(1)'}(t^{''})|\Psi_I(t^{'})>
\end{aligned}$$

$$\boxed{|\Psi_I(t)>=|\Psi_I(t_0)>+\tfrac{1}{i\hbar}\textstyle\int_{t_0}^{t}dt^{'}H^{(1)'}|\Psi_I(t_0)>+\tfrac{1}{(i\hbar)^2}\textstyle\int_{t_0}^{t}dt^{'}\int_{t_0}^{t^{'}}dt^{''}H^{(1)'}(t^{'})H^{(1)'}(t^{''})|\Psi_I(t^{'})>} \tag{26.5}$$

This is the wavefunction corrected to 2nd order.

Iteration 2

Like in the previous case, take the expresion $|\Psi_I(t)>=|\Psi_I(t_0)>+\frac{1}{i\hbar}\int_{t_0}^{t}dt^{'}H^{(1)'}|\Psi_I(t^{'})>$ and replace it into the back part of the 2nd order expression above.

$$\begin{aligned}
|\Psi_I(t)> &= |\Psi_I(t_0)>+\frac{1}{i\hbar}\int_{t_0}^{t}dt^{'}H^{(1)'}|\Psi_I(t_0)> \\
&+ \frac{1}{(i\hbar)^2}\int_{t_0}^{t}dt^{'}\int_{t_0}^{t^{'}}dt^{''}H^{(1)'}H^{(1)''}\left[|\Psi_I(t_0)>+\frac{1}{i\hbar}\int_{t_0}^{t^{''}}dt^{'''}H^{(1)'}(t^{'''})|\Psi_I(t^{'''})>\right] \\
|\Psi_I(t)> &= |\Psi_I(t_0)>+\frac{1}{i\hbar}\int_{t_0}^{t}dt^{'}H^{(1)'}|\Psi_I(t_0)> \\
&+ \frac{1}{(i\hbar)^2}\int_{t_0}^{t}dt^{'}\int_{t_0}^{t^{'}}dt^{''}H^{(1)'}(t^{'})H^{(1)'}(t^{''})|\Psi_I(t_0)> \\
&+ \frac{1}{(i\hbar)^3}\int_{t_0}^{t}dt^{'}\int_{t_0}^{t^{'}}dt^{''}H^{(1)'}(t^{'})H^{(1)'}(t^{''})\int_{t_0}^{t^{''}}dt^{'''}H^{(1)'}(t^{'''})|\Psi_I(t^{'''})>
\end{aligned}$$

$$\begin{aligned}
|\Psi_I(t)> &= |\Psi_I(t_0)>+\frac{1}{i\hbar}\int_{t_0}^{t}dt^{'}H^{(1)'}|\Psi_I(t_0)> \\
&+ \frac{1}{(i\hbar)^2}\int_{t_0}^{t}dt^{'}\int_{t_0}^{t^{'}}dt^{''}H^{(1)'}(t^{'})H^{(1)'}(t^{''})|\Psi_I(t_0)> \\
&+ \frac{1}{(i\hbar)^3}\int_{t_0}^{t}dt^{'}\int_{t_0}^{t^{'}}dt^{''}\int_{t_0}^{t^{''}}dt^{'''}H^{(1)'}(t^{'})H^{(1)'}(t^{''})H^{(1)'}(t^{'''})|\Psi_I(t^{'''})>
\end{aligned} \tag{26.6}$$

This is the wavefunction corrected to 3rd order.

Iteration 3

Continue in the same manner to get higher order corrections. For the 4th order correction:

$$\begin{aligned}
& |\Psi_I(t) >= |\Psi_I(t_0) > + \frac{1}{i\hbar}\int_{t_0}^{t} dt^{'} H^{(1)'} |\Psi_I(t_0) > \\
+ & \frac{1}{(i\hbar)^2}\int_{t_0}^{t} dt^{'} \int_{t_0}^{t^{'}} dt^{''} H^{(1)'}(t^{'}) H^{(1)'}(t^{''}) |\Psi_I(t_0) > \\
+ & \frac{1}{(i\hbar)^3}\int_{t_0}^{t} dt^{'} \int_{t_0}^{t^{'}} dt^{''} \int_{t_0}^{t^{''}} dt^{'''} H^{(1)'}(t^{'}) H^{(1)'}(t^{''}) H^{(1)'}(t^{'''}) \cdot \\
& \left[|\Psi_I(t_0) > + \frac{1}{i\hbar}\int_{t_0}^{t^{'''}} dt^{''''} H^{(1)'}(t^{''''}) |\Psi_I(t^{''''}) > \right]
\end{aligned}$$

$$\begin{aligned}
& |\Psi_I(t) >= |\Psi_I(t_0) > + \frac{1}{i\hbar}\int_{t_0}^{t} dt^{'} H^{(1)'} |\Psi_I(t_0) > \\
+ & \frac{1}{(i\hbar)^2}\int_{t_0}^{t} dt^{'} \int_{t_0}^{t^{'}} dt^{''} H^{(1)'}(t^{'}) H^{(1)'}(t^{''}) |\Psi_I(t_0) > \\
+ & \frac{1}{(i\hbar)^3}\int_{t_0}^{t} dt^{'} \int_{t_0}^{t^{'}} dt^{''} \int_{t_0}^{t^{''}} dt^{'''} H^{(1)'}(t^{'}) H^{(1)'}(t^{''}) H^{(1)'}(t^{'''}) |\Psi_I(t_0) > \\
+ & \frac{1}{(i\hbar)^4}\int_{t_0}^{t} dt^{'} \int_{t_0}^{t^{'}} dt^{''} \int_{t_0}^{t^{''}} dt^{'''} H^{(1)'}(t^{'}) H^{(1)'}(t^{''}) H^{(1)'}(t^{'''}) \int_{t_0}^{t^{'''}} dt^{'''} H^{(1)'}(t^{''''}) |\Psi_I(t^{''''}) >
\end{aligned}$$

$$\begin{aligned}
|\Psi_I(t) > \quad = \quad & |\Psi_I(t_0) > + \frac{1}{i\hbar}\int_{t_0}^{t} dt^{'} H^{(1)'} |\Psi_I(t_0) > \\
+ & \frac{1}{(i\hbar)^2}\int_{t_0}^{t} dt^{'} \int_{t_0}^{t^{'}} dt^{''} H^{(1)'}(t^{'}) H^{(1)'}(t^{''}) |\Psi_I(t_0) > \\
+ & \frac{1}{(i\hbar)^3}\int_{t_0}^{t} dt^{'} \int_{t_0}^{t^{'}} dt^{''} \int_{t_0}^{t^{''}} dt^{'''} H^{(1)'}(t^{'}) H^{(1)'}(t^{''}) H^{(1)'}(t^{'''}) |\Psi_I(t_0) > \\
+ & \frac{1}{(i\hbar)^4}\int_{t_0}^{t} dt^{'} \int_{t_0}^{t^{'}} dt^{''} \int_{t_0}^{t^{''}} dt^{'''} \int_{t_0}^{t^{'''}} dt^{''''} H^{(1)'}(t^{'}) H^{(1)'}(t^{''}) H^{(1)'}(t^{'''}) H^{(1)'}(t^{''''}) |\Psi_I(t^{''''}) >
\end{aligned} \tag{26.7}$$

This is the wavefunction corrected to 4th order.

Summary

You can go on forever in this fashion to get even higher order solutions. Note that the form of the expression is basically what we derived earlier where we split $e^{i\omega_{kn}t}$ after the fact and changed $H^{(1)} \rightarrow H^{(1)'}$ except we didn't derive this in an ad hoc fashion.

$$\boxed{|\Psi_I(t_0)>} \tag{26.8}$$

$$\boxed{|\Psi_I(t_0)> + \frac{1}{i\hbar}\int_{t_0}^{t} d^{'}H^{(1)'}|\Psi_I(t_0)>} \tag{26.9}$$

$$\boxed{|\Psi_I(t_0)> + \frac{1}{i\hbar}\int_{t_0}^{t} d^{'}H^{(1)'}|\Psi_I(t_0)> + \frac{1}{(i\hbar)^2}\int_{t_0}^{t} dt^{'}\int_{t_0}^{t^{'}} dt^{''}H^{(1)'}(t^{'})H^{(1)'}(t^{''})|\Psi_I(t_0)>} \tag{26.10}$$

These are the zeroth, first and second order corrections

$$\begin{aligned}
|\Psi_I(t_0)> &= |\Psi_I(t_0)> + \frac{1}{i\hbar}\int_{t_0}^{t} d^{'}H^{(1)'}|\Psi_I(t_0)> \\
&+ \frac{1}{(i\hbar)^2}\int_{t_0}^{t} dt^{'}\int_{t_0}^{t^{'}} dt^{''}H^{(1)'}(t^{'})H^{(1)'}(t^{''})|\Psi_I(t_0)> \\
&+ \frac{1}{(i\hbar)^3}\int_{t_0}^{t} dt^{'}\int_{t_0}^{t^{'}} dt^{''}\int_{t_0}^{t^{''}} dt^{'''}H^{(1)'}(t^{'})H^{(1)'}(t^{''})H^{(1)'}(t^{'''})|\Psi_I(t_0)>
\end{aligned} \tag{26.11}$$

This is the solution up to third order in correction.

Now we can find the time dependent coefficients $C(t)$ as well as $P(t)$, the transition probability in the usual manner. Multiply and integrate both sides of the previous wavefunctions by $< k|$ for example (which is basically the $t = 0$ Schrodinger or Interaction wavefunction and is one of the unperturbed basis set).

$$\begin{aligned}
C_k^{(1)} &= < k|\frac{1}{i\hbar}\int_{t_0}^{t} dt^{'}H^{(1)'}|\Psi_I(t_0)> \\
&= \delta_k
\end{aligned}$$

This is our zeroth order solution.

Next

$$\begin{aligned} C_k^{(1)} &= < k|\frac{1}{i\hbar}\int_{t_0}^{t} dt^{'} H^{(1)'}(t^{'})|\Psi_I(t_0) > \\ &= \frac{1}{i\hbar}\int_{t_0}^{t} dt^{'} < k|H^{(1)'}(t^{'})|\Psi_I(t_0) > \end{aligned}$$

This is our first order solution. And so forth...

Probabilities are determined in the usual fashion

$$\begin{aligned} P_k &= |C_k|^2 \\ R &= \frac{dP_k}{dt} \end{aligned}$$

Finally, to define the operator in the interaction representation simply note that the expectation values will have the same form as in either the Schrodinger or Heisenber representations. Therefore for a generic operator A

$$\begin{aligned} < A > &= < \Psi_s|A_s|\Psi_s > \\ &= < \Psi_I|e^{\frac{iH^{(0)}t}{\hbar}} A_s e^{\frac{-iH^{(0)}t}{\hbar}}|\Psi_I > \\ &= < \Psi_I|A_I|\Psi_I > \end{aligned}$$

So

$$A_I = e^{\frac{iH^{(0)}t}{\hbar}} A_s e^{\frac{-iH^{(0)}t}{\hbar}}$$

and where we utilized the definition

$$|\Psi_I >= e^{\frac{iH^{(0)}t}{\hbar}}|\Psi_s >$$

$$|\Psi_s >= e^{\frac{-iH^{(0)}t}{\hbar}}|\Psi_I >$$

Chapter 27

Two level system revisited

Two level systems revisited

Before we go on with the interaction representation formalism and time dependent perturbation theory let's revisit our favorite 2-level system in the interaction representation and *solve it* without invoking time dependent perturbation theory.

We should get the same solution as in the Schrödinger representation.

Call the initial state n and the final state k like usual.

Consider a harmonic perturbation

$$H^{(1)}(t) = -\overrightarrow{\mu} \cdot \overrightarrow{\epsilon} = -\mu\epsilon_0 \sin\omega t \tag{27.1}$$

(Schrödinger representation)

where we will take the z component as usual.

$$H^{(1)}(t) = -\mu_z\epsilon_0 \sin\omega t \tag{27.2}$$

(Schrödinger representation)

Furthermore recall that in the interaction representation

$$H'^{(1)}(t) = e^{\frac{iH_0 t}{\hbar}} H^{(1)}(t) e^{-\frac{iH_0 t}{\hbar}} \tag{27.3}$$

Finally recall that the wavefunction in either the Schrödinger or interaction representation can be expressed as a linear combination of n and k with time dependent coefficients. Since we are working in the interaction representation we will express $|\psi(t)\rangle_I$ as a sum of $|\psi_n\rangle_I$ and $|\psi_k\rangle_I$ with time dependent coefficients $C_n(t)$ and $C_k(t)$

$$|\psi(t)\rangle_I = C_n(t)|\psi_n\rangle_I + C_k(t)|\psi_k\rangle_I \tag{27.4}$$

but $|\psi_n\rangle_I = |\psi_n\rangle_S$ at $t = 0$ and $|\psi_n\rangle_I = |\psi_n\rangle_S$.

The "I" is to explicitly remind you that we are in the interaction representation. We are *not* in the Schrödinger representation. Furthermore recall that

$$|\psi(t)\rangle_I = e^{\frac{iH_0 t}{\hbar}}|\psi(t)\rangle_S \tag{27.5}$$

so be careful.

Finally our Schrödinger equation in the interaction representation is

$$i\hbar\frac{d|\psi_I(t)\rangle}{dt} = H'^{(1)}|\psi_I(t)\rangle \tag{27.6}$$

Now that we have all of that squared away let's go and evaluate our system of coupled differential equations just like in the Schrödinger representation case. First our expression for $\frac{dC_k(t)}{dt}$.

Project $\langle k|$ onto our interaction picture Schrödinger equation

$$\langle k|\left[i\hbar\frac{d|\psi_I(t)\rangle}{dt}\right] = \langle k|\left[H'^{(1)}|\psi_I(t)\rangle\right]$$

Let $C_n(t) \equiv C_n$ and $C_k(t) \equiv C_k$.

$$\begin{aligned}
i\hbar\frac{d\langle k|\psi_I(t)\rangle}{dt} &= \langle k|H'^{(1)}|\left[C_n|n\rangle + C_k|k\rangle\right] \\
&= C_n\langle k|H'^{(1)}|n\rangle + C_k\langle k|H'^{(1)}|k\rangle \\
i\hbar\frac{d}{dt}\langle k|\left[C_n|n\rangle + C_k|k\rangle\right] &= C_n\langle k|H'^{(1)}|n\rangle + C_k\langle k|H'^{(1)}|k\rangle \\
i\hbar\frac{d}{dt}\left[C_n\langle k|n\rangle + C_k\langle k|k\rangle\right] &= C_n\langle k|H'^{(1)}|n\rangle + C_k\langle k|H'^{(1)}|k\rangle \\
i\hbar\frac{dC_k}{dt} &= C_n\langle k|H'^{(1)}|n\rangle + C_k\langle k|H'^{(1)}|k\rangle
\end{aligned}$$

where now recall

$$\boxed{H'^{(1)} = \left(e^{\frac{iH_0 t}{\hbar}}H^{(1)}(t)e^{-\frac{iH_0 t}{\hbar}}\right)} \tag{27.7}$$

$$\begin{aligned}
i\hbar\frac{dC_k}{dt} &= C_n\langle k|e^{\frac{iH_0t}{\hbar}}H^{(1)}(t)e^{-\frac{iH_0t}{\hbar}}|n\rangle + C_k\langle k|e^{\frac{iH_0t}{\hbar}}H^{(1)}(t)e^{-\frac{iH_0t}{\hbar}}|k\rangle \\
i\hbar\frac{dC_k}{dt} &= C_n e^{\frac{i\epsilon_k^{(0)}t}{\hbar}}\langle k|H^{(1)}(t)|n\rangle e^{-\frac{i\epsilon_n^{(0)}t}{\hbar}} + C_k e^{\frac{i\epsilon_k^{(0)}t}{\hbar}}\langle k|H^{(1)}(t)|k\rangle e^{-\frac{i\epsilon_k^{(0)}t}{\hbar}} \\
i\hbar\frac{dC_k}{dt} &= C_n e^{\frac{i(\epsilon_k^{(0)}-\epsilon_n^{(0)})t}{\hbar}}\langle k|H^{(1)}(t)|n\rangle + C_k\langle k|H^{(1)}(t)|k\rangle
\end{aligned}$$

Use $\omega_{kn} = (\epsilon_k^{(0)} - \epsilon_n^{(0)})\hbar$ to convert this expression to

$$i\hbar\frac{dC_k}{dt} = C_n e^{i\omega_{kn}t}\langle k|H^{(1)}(t)|n\rangle + C_k\langle k|H^{(1)}(t)|k\rangle$$

Now express $H^{(1)} = -\mu_z\epsilon_0\sin\omega t$

$$\begin{aligned}
i\hbar\frac{dC_k}{dt} &= C_n e^{i\omega_{kn}t}\langle k| - \mu_z\epsilon_0\sin\omega t|n\rangle + C_k\langle k| - \mu_z\epsilon_0\sin\omega t|k\rangle \\
i\hbar\frac{dC_k}{dt} &= -\epsilon_0\sin\omega t\left[C_n e^{i\omega_{kn}t}\langle k|\mu_z|n\rangle + C_k\langle k|\mu_z|k\rangle\right]
\end{aligned}$$

$$\boxed{i\hbar\frac{dC_k}{dt} = -\epsilon_0\left[C_n e^{i\omega_{kn}t}\langle k|\mu_z|n\rangle + C_k\langle k|\mu_z|k\rangle\right]\left(\frac{e^{i\omega t}-e^{-i\omega t}}{2i}\right)} \qquad (27.8)$$

This is the desired expression for C_k.

Now repeat the entire process to get an equivalent expression for C_n. Project $|n>$ onto our interaction picture Schrödinger equation

$$\begin{aligned}
\langle n|\left[\frac{i\hbar d|\psi_I(t)\rangle}{dt}\right] &= \langle n|\left[H'^{(1)}|\psi_I(t)\rangle\right] \\
i\hbar\frac{d}{dt}\langle n|\psi_I(t)\rangle &= \langle n|H'^{(1)}|\left[C_n|n\rangle + C_k|k\rangle\right] \\
i\hbar\frac{d}{dt}\langle n|\psi_I(t)\rangle &= C_n\langle n|H'^{(1)}|n\rangle + C_k\langle n|H'^{(1)}|k\rangle \\
i\hbar\frac{d}{dt}\langle n|\left[C_n|n\rangle + C_k|k\rangle\right] &= C_n\langle n|H'^{(1)}|n\rangle + C_k\langle n|H'^{(1)}|k\rangle \\
i\hbar\frac{d}{dt}\left[C_n\langle n|n\rangle + C_k\langle n|k\rangle\right] &= C_n\langle n|H'^{(1)}|n\rangle + C_k\langle n|H'^{(1)}|k\rangle \\
i\hbar\frac{dC_n}{dt} &= C_n\langle n|H'^{(1)}|n\rangle + C_k\langle n|H'^{(1)}|k\rangle \\
i\hbar\frac{dC_n}{dt} &= C_n\langle n|e^{\frac{iH_0t}{\hbar}}H^{(1)}(t)e^{-\frac{iH_0t}{\hbar}}|n\rangle + C_k\langle n|e^{\frac{iH_0t}{\hbar}}H^{(1)}(t)e^{-\frac{iH_0t}{\hbar}}|k\rangle \\
i\hbar\frac{dC_n}{dt} &= C_n e^{\frac{i\epsilon_n^{(0)}t}{\hbar}}\langle n|H^{(1)}|n\rangle e^{-\frac{i\epsilon_n^{(0)}t}{\hbar}} + C_k e^{\frac{i\epsilon_n^{(0)}t}{\hbar}}\langle n|H^{(1)}|n\rangle e^{-\frac{i\epsilon_n^{(0)}t}{\hbar}} \\
i\hbar\frac{dC_n}{dt} &= C_n\langle n|H^{(1)}|n\rangle + C_k e^{\frac{i\left(\epsilon_n^{(0)}-\epsilon_k^{(0)}\right)t}{\hbar}}\langle n|H^{(1)}|n\rangle \\
i\hbar\frac{dC_n}{dt} &= C_n\langle n|H^{(1)}|n\rangle + C_k e^{-i\omega_{kn}t}\langle n|H^{(1)}|n\rangle \\
i\hbar\frac{dC_n}{dt} &= C_n\langle n| - \mu_z\epsilon_0\sin\omega t|n\rangle + C_k e^{-i\omega_{kn}t}\langle n| - \mu_z\epsilon_0\sin\omega t|n\rangle \\
i\hbar\frac{dC_n}{dt} &= -\epsilon_0\sin\omega t\left[C_n\langle n|\mu_z|n\rangle + C_k e^{-i\omega_{kn}t}\langle n|\mu_z|n\rangle\right]
\end{aligned}$$

resulting in

$$\boxed{i\hbar\frac{dC_n}{dt} = -\epsilon_0\left[C_n\langle n|\mu_z|n\rangle + C_k e^{-i\omega_{kn}t}\langle n|\mu_z|n\rangle\right]\left(\frac{e^{i\omega t}-e^{-i\omega t}}{2i}\right)} \qquad (27.9)$$

This is the desired expression for C_n.

Now summarize the two coupled differential equations

$$\boxed{i\hbar\frac{dC_n}{dt} = -\epsilon_0\left[C_n\langle n|\mu_z|n\rangle + C_k e^{-i\omega_{kn}t}\langle n|\mu_z|k\rangle\right]\left(\frac{e^{i\omega t}-e^{-i\omega t}}{2i}\right)} \qquad (27.10)$$

$$\boxed{i\hbar\frac{dC_k}{dt} = -\epsilon_0\left[C_n e^{i\omega_{kn}t}\langle k|\mu_z|n\rangle + C_k\langle k|\mu_z|k\rangle\right]\left(\frac{e^{i\omega t}-e^{-i\omega t}}{2i}\right)} \qquad (27.11)$$

Now we need some more simplification:

$$\begin{aligned}
i\hbar\frac{dC_n}{dt} &= -\frac{\epsilon_0}{2i}\left[C_n\langle n|\mu_z|n\rangle\left(e^{i\omega t}-e^{-i\omega t}\right)+C_k e^{-i\omega_{kn}t}\langle n|\mu_z|k\rangle\left(e^{i\omega t}-e^{-i\omega t}\right)\right] \\
i\hbar\frac{dC_k}{dt} &= -\frac{\epsilon_0}{2i}\left[C_n e^{i\omega_{kn}t}\langle k|\mu_z|n\rangle\left(e^{i\omega t}-e^{-i\omega t}\right)+C_k\langle k|\mu_z|k\rangle\left(e^{i\omega t}-e^{-i\omega t}\right)\right] \\
i\hbar\frac{dC_n}{dt} &= -\frac{\epsilon_0}{2i}\left[C_n\langle n|\mu_z|n\rangle\left(e^{i\omega t}-e^{-i\omega t}\right)+C_k\langle n|\mu_z|k\rangle\left(e^{i(\omega-\omega_{kn})t}-e^{-i(\omega+\omega_{kn})t}\right)\right] \\
i\hbar\frac{dC_k}{dt} &= -\frac{\epsilon_0}{2i}\left[C_n\langle k|\mu_z|n\rangle\left(e^{i(\omega+\omega_{kn})t}-e^{-i(\omega-\omega_{kn})t}\right)+C_k\langle k|\mu_z|k\rangle\left(e^{i\omega t}-e^{-i\omega t}\right)\right]
\end{aligned}$$

Now certain coefficients of $C_n(t)$ and $C_k(t)$ are proportional to $e^{\pm i(\omega-\omega_{kn})t}$ so they oscillate slowly in time when $\omega \approx \omega_{kn}$. The other coefficients proportional to either $e^{\pm i\omega t}$ or $e^{\pm i(\omega+\omega_{kn})t}$ oscillate more rapidly. The *secular approximation* or AKA *rotating wave approximation* consists of neglecting the rapidly oscillating terms. Alternatively, a parity argument can be invoked where $< n|\mu_z|n > \simeq 0$ and $< k|\mu_z|k > \simeq 0$.

The remaining terms are called *secular terms* and dominate contributions to C_n or C_k.

$$\begin{aligned}
i\hbar\frac{dC_n}{dt} &= -\frac{\epsilon_0}{2i}\left[C_k\langle n|\mu_z|k\rangle e^{i(\omega-\omega_{kn})t}\right] \\
i\hbar\frac{dC_k}{dt} &= +\frac{\epsilon_0}{2i}\left[C_n\langle n|\mu_z|k\rangle e^{-i(\omega-\omega_{kn})t}\right]
\end{aligned}$$

or

$$\begin{aligned}
\frac{dC_n}{dt} &= \frac{\epsilon_0}{2\hbar}\left[C_k\langle n|\mu_z|k\rangle e^{i(\omega-\omega_{kn})t}\right] \\
\frac{dC_k}{dt} &= -\frac{\epsilon_0}{2\hbar}\left[C_n\langle k|\mu_z|n\rangle e^{-i(\omega-\omega_{kn})t}\right]
\end{aligned}$$

Now if you are *exactly* at resonance $\omega = \omega_{kn}$

$$\begin{aligned}
\frac{dC_n}{dt} &= \frac{\epsilon_0}{2\hbar}C_k\langle n|\mu_z|k\rangle \\
\frac{dC_k}{dt} &= -\frac{\epsilon_0}{2\hbar}C_n\langle k|\mu_z|n\rangle
\end{aligned}$$

Now differentiate the first expression and substitute the result into the second

$$\begin{aligned}
\frac{d^2C_n}{dt^2} &= \frac{\epsilon_0}{2\hbar}\langle n|\mu_z|k\rangle\frac{dC_k}{dt} \\
\frac{dC_k}{dt} &= \frac{2\hbar}{\epsilon_0\langle n|\mu_z|k\rangle}\frac{d^2C_n}{dt^2} \\
\frac{2\hbar}{\epsilon_0\langle n|\mu_z|k\rangle}\frac{d^2C_n}{dt^2} &= -\frac{\epsilon_0}{2\hbar}C_n\langle k|\mu_z|n\rangle \\
\frac{d^2C_n}{dt^2} &= -\frac{\epsilon_0^2}{4\hbar^2}\left|\langle k|\mu_z|n\rangle\right|^2 C_n
\end{aligned}$$

Now we apply the boundary conditions of the problem. The system initially starts in the state n:

$$\begin{aligned}
C_n(0) &= 1 \\
C_k(0) &= 0
\end{aligned}$$

The solution to our second order differential equation which satisfies the initial boundary conditions is

$$\boxed{C_n(t) = \cos\left(\frac{\epsilon_0\langle k|\mu_z|n\rangle t}{2\hbar}\right)} \tag{27.12}$$

From which we get

$$\boxed{P_n = |C_n(t)|^2 = \cos^2\left(\frac{\epsilon_0\langle k|\mu_z|n\rangle t}{2\hbar}\right)} \tag{27.13}$$

To find the counterpart values for $C_k(t)$ and P_k use the above $C_n(t)$ expression in

$$\begin{aligned}
\frac{dC_k(t)}{dt} &= -\frac{\epsilon_0}{2\hbar}\langle k|\mu_z|n\rangle C_n(t) \\
\frac{dC_k(t)}{dt} &= -\frac{\epsilon_0}{2\hbar}\langle k|\mu_z|n\rangle\cos\left(\frac{\epsilon_0\langle k|\mu_z|n\rangle t}{2\hbar}\right)
\end{aligned}$$

Integrate:

$$\boxed{C_k(t) = -\sin\left(\frac{\epsilon_0\langle k|\mu_z|n\rangle t}{2\hbar}\right)} \tag{27.14}$$

and from this

$$\boxed{P_k = \sin^2\left(\frac{\epsilon_0\langle k|\mu_z|n\rangle t}{2\hbar}\right)} \tag{27.15}$$

Summary

$$\boxed{P_n = \cos^2\left(\frac{\epsilon_0\langle k|\mu_z|n\rangle t}{2\hbar}\right)} \tag{27.16}$$

$$\boxed{P_k = \sin^2\left(\frac{\epsilon_0\langle k|\mu_z|n\rangle t}{2\hbar}\right)} \tag{27.17}$$

These are exactly identical to the solutions found previously in the Schrödinger representation.

Chapter 28

1st order transitions, Interaction representation

Now that we have re-expressed everything in the interaction representation, let's find the transition probability to a final state (say k) after the time dependent perturbation has been turned on. (We did this before through the Schrodinger representation-we'll do it again here) The bottom line however, is the final results should not be different.

Recall from before that the state function in the interaction representation was

$$|\Psi(t)>=|\Psi(t_0)>+\frac{1}{i\hbar}\int_{t_0}^{t}dt^{'}H^{(1)^{'}}|\Psi(t_0)>$$

to first order. Recall also that $|\Psi_I(t_0)>=|\Psi_s(t_0)>$ so we will drop the I and S subscripts for notational convenience.

Now to find out the time dependent coefficient $C_k(t)$ we project $<\Psi_k|$ or $<k|$ onto the perturbed state function.

$$\boxed{C_k(t)=<k|\Psi(t)>} \tag{28.1}$$

from which we can get the transition probability through

$$P_k=|C_k(t)|^2$$

Let's get started

$$C_k(t)=<k|[\Psi(t_0)>+\frac{1}{i\hbar}\int_{t_0}^{t}dt^{'}H^{(1)^{'}}|\Psi(t_0)>]$$

For convenience call the initial state n.

$$|\Psi(t_0) >= |n >$$

$$\begin{aligned} C_k(t) &= < k| \left[|n > + \frac{1}{i\hbar} \int_{t_0}^{t} dt' H^{(1)'} |n > \right] \\ &= < k|n > + \frac{1}{i\hbar} \int_{t_0}^{t} dt' < k|H^{(1)'}|n > \\ &= \delta_{kn} + \frac{1}{i\hbar} \int_{t_0}^{t} dt' < k|H^{(1)'}|n > \end{aligned}$$

$$\boxed{C_k(t) = \frac{1}{i\hbar} \int_{t_0}^{t} dt' < k|H^{(1)'}|n >} \tag{28.2}$$

This is our expression for the time dependent coefficient in the interaction representation.

Now we could just stop here but we should also recall that since we are in the interaction representation $H^{(1)'}(t)$ is hiding some extra piece of information. Recall that

$$H^{(1)'} = e^{\frac{iH^{(0)}t}{\hbar}} H^{(1)} e^{\frac{-iH^{(0)}t}{\hbar}}$$

Replace this back into the above expression.

$$C_k(t) = \frac{1}{i\hbar} \int_{t_0}^{t} dt' < k|e^{\frac{iH^{(0)}t'}{\hbar}} H^{(1)} e^{\frac{-iH^{(0)}t'}{\hbar}} |n >$$

Furthermore we know from before that

$$e^{\frac{-iH^{(0)}t}{\hbar}} |n >= e^{\frac{-i\epsilon_n t}{\hbar}} |n >$$

therefore

$$C_k(t) = \frac{1}{i\hbar} \int_{t_0}^{t} dt' e^{\frac{i\epsilon_k^{(0)}t'}{\hbar}} < k|H^{(1)}|n > e^{\frac{-i\epsilon_n^{(0)}t'}{\hbar}}$$

(note that the prime is gone over the H term inside the bra-ket).

$$C_k(t) = \frac{1}{i\hbar} \int_{t_0}^{t} dt' e^{\frac{i(\epsilon_k^{(0)} - \epsilon_n^{(0)})t'}{\hbar}} < k|H^{(1)}|n >$$

where we let $\omega_{kn} = \frac{(\epsilon_k - \epsilon_n)}{\hbar}$.

$$\boxed{C_k(t) = \frac{1}{i\hbar}\int_{t_0}^{t} dt^{'} e^{i\omega_{kn}t^{'}} < k|H^{(1)}|n >} \tag{28.3}$$

This is our desired time dependent coefficient. Note that it should be identical to the expression we derived within the Schrodinger representation.

Now if we want the general expression for the transition probability we apply

$$P_k = |C_k(t)|^2$$

$$\boxed{P_k = \frac{1}{\hbar^2}|\int_{t_0}^{t} e^{i\omega_{kn}t^{'}} < k|H^{(1)}|n > |^2} \tag{28.4}$$

This is the general expression for the transition probability to first order.

Now we will run through some more specific problems. Derive the transition probabilities of the following problems. We will let $t_0 = 0$ for convenience.

- $H^{(1)}$ =constant, time independent
- $H^{(1)} \propto sin\omega t$ this one is new
- $H^{(1)} \propto cos\omega t$ we did this one before

Example 1, $H^{(1)}$ constant

$$\begin{aligned}
P_k &= \frac{1}{\hbar^2}\left|\int_{t_0}^{t} dt^{'} e^{i\omega_{kn}t^{'}} < k|H^{(1)}|n >\right|^2 \\
&= \frac{| < k|H^{(1)}|n > |^2}{\hbar^2}\left|\int_{t_0}^{t} dt^{'} e^{i\omega_{kn}t^{'}}\right|^2 \\
&= \frac{| < k|H^{(1)}|n > |^2}{\hbar^2}\left|\frac{e^{i\omega_{kn}t} - e^{i\omega_{kn}t_0}}{i\omega_{kn}}\right|^2 \\
&\quad \text{let } t_0 = 0 \text{ for simplicity} \\
&= \frac{| < k|H^{(1)}|n > |^2}{\hbar^2}\left|\frac{e^{i\omega_{kn}t} - 1}{i\omega_{kn}}\right|^2
\end{aligned}$$

Do the last term separately

$$\begin{aligned}\left(\frac{e^{i\omega_{kn}t}-1}{i\omega_{kn}}\right) &= \frac{e^{\frac{i\omega_{kn}t}{2}}}{i\omega_{kn}}\left(e^{\frac{i\omega_{kn}t}{2}}-e^{\frac{-i\omega_{kn}t}{2}}\right)\\ &= \frac{2e^{i\omega_{kn}t}}{\omega_{kn}}\left(\frac{e^{\frac{i\omega_{kn}t}{2}}-e^{\frac{-i\omega_{kn}t}{2}}}{2i}\right)\\ &= \frac{2e^{i\omega_{kn}t}}{\omega_{kn}}sin\frac{\omega_{kn}t}{2}\end{aligned}$$

Now square this

$$\left|\frac{2e^{i\omega_{kn}t}}{\omega_{kn}}sin\frac{\omega_{kn}t}{2}\right|^2 = \frac{4}{\omega_{kn}^2}sin^2\frac{\omega_{kn}t}{2}$$

Putting it all together we get

$$P_k = \frac{|<k|H^{(1)}|n>|^2}{\hbar^2}\left(\frac{4}{\omega_{kn}^2}\right)sin^2\frac{\omega_{kn}t}{2}$$

$$\boxed{P_k = \tfrac{4|<k|H^{(1)}|n>|^2}{\hbar^2}\left(\frac{sin^2\frac{\omega_{kn}t}{2}}{\omega_{kn}^2}\right)} \tag{28.5}$$

Example 2, $H^{(1)} \propto sin\omega t$

Consider a harmonic perturbation. We will express $H^{(1)}(t)$ much like we did for light just so our final expressions can be compared to our previous results.

$$H^{(1)} = -\mu\cdot\epsilon_0 sin\omega t$$

Take the z component for convenience.

$$H^{(1)} = -\mu_z\epsilon_0 sin\omega t$$

The transition probability is

$$\begin{aligned}
P_k &= \frac{1}{\hbar^2}\left|\int_{t_0}^{t} dt^{'} e^{i\omega_{kn}t} < k|H^{(1)}|n >\right|^2 \\
&= \frac{1}{\hbar^2}\left|\int_{t_0}^{t} dt^{'} e^{i\omega_{kn}t^{'}} < k| -\mu_z\epsilon_0 sin\omega t^{'}|n >\right|^2 \\
&= \frac{1}{\hbar^2}\left|\int_{t_0}^{t} dt^{'} e^{i\omega_{\omega_{kn}}t^{'}}(-\epsilon_0)sin\omega t^{'} < k|\mu_z|n >\right|^2 \\
&= \frac{\epsilon_0^2| < k|\mu_z|n > |^2}{\hbar^2}\left|\int_{t_0}^{t} dt^{'} e^{i\omega_{kn}t^{'}} sin\omega t^{'}\right|^2 \\
&= \frac{\epsilon_0^2| < k|\mu_z|n > |^2}{\hbar^2}\left|\int_{t_0}^{t} dt^{'} e^{i\omega_{kn}t^{'}}(\frac{e^{i\omega t^{'}} - e^{-i\omega t^{'}}}{2i})\right|^2 \\
&= \frac{\epsilon_0^2| < k|\mu_z|n > |^2}{4\hbar^2}\left|\int_{t_0}^{t} e^{i\omega_{kn}t^{'}}(e^{i\omega t} - e^{-i\omega t})\right|^2 \\
&= \frac{\epsilon_0^2| < k|\mu_z|n > |^2}{4\hbar^2}\left|\int_{t_0}^{t} e^{i(\omega_{kn}+\omega)t^{'}} - e^{i(\omega_{kn}-\omega)t^{'}}\right|^2
\end{aligned}$$

Ok at this point for convenience let's consider the last term separately and evaluate it.

$$\begin{aligned}
\int_{t_0}^{t} dt^{'} e^{i(\omega_{kn}+\omega)t^{'}} - e^{i(\omega_{kn}-\omega)t^{'}} &= \frac{(e^{i(\omega_{kn}+\omega)t} - e^{i(\omega_{kn}+\omega)t_0})}{i(\omega_{kn}+\omega)} \\
&- \frac{(e^{i(\omega_{kn}-\omega)t} - e^{i(\omega_{kn}-\omega)t_0})}{i(\omega_{kn}-\omega)}
\end{aligned}$$

Let $t_0 = 0$ for convenience.

$$= \left(\frac{e^{i(\omega_{kn}+\omega)t} - 1}{i(\omega_{kn}+\omega)}\right) - \left(\frac{e^{i(\omega_{kn}-\omega)t} - 1}{i(\omega_{kn}-\omega)}\right)$$

Now take the Rotating wave approximation and drop the 1st term.

$$= -\left(\frac{e^{i(\omega_{kn}-\omega)t} - 1}{i(\omega_{kn}-\omega)}\right)$$

Extract out $e^{\frac{i(\omega_{kn}-\omega)t}{2}}$

$$\begin{aligned}
& -e^{\frac{i(\omega_{kn}-\omega)t}{2}}\left(\frac{e^{\frac{i(\omega_{kn}-\omega)t}{2}}-e^{\frac{-i(\omega_{kn}-\omega)t}{2}}}{i(\omega_{kn}-\omega)}\right) \\
= & -2e^{\frac{i(\omega_{kn}-\omega)t}{(\omega_{kn}-\omega)}}\left(\frac{e^{\frac{i(\omega_{kn}-\omega)t}{2}}-e^{\frac{-i(\omega_{kn}-\omega)t}{2}}}{2i}\right) \\
= & -\frac{2e^{\frac{i(\omega_{kn}-\omega)t}{2}}}{(\omega_{kn}-\omega)} sin\frac{(\omega_{kn}-\omega)t}{2}
\end{aligned}$$

Now square this term and replace it back into the main expression

$$= \frac{\epsilon_0^2|<k|\mu_z|n>|^2}{4\hbar^2}\frac{4}{(\omega_{kn}-\omega)^2}sin^2\frac{(\omega_{kn}-\omega)t}{2}$$

$$\boxed{P_k = \frac{\epsilon_0^2|<k|\mu_z|n>|^2}{\hbar^2}\left(\frac{sin^2\frac{(\omega_{kn}-\omega)t}{2}}{(\omega_{kn}-\omega)^2}\right)} \qquad (28.6)$$

Expression for desired transition probability with sinusoidal perturbation. This should look a little familiar. (same as with cosine perturbation which we had been assuming all along).

Example 3, $H^{(1)} \propto cos\omega t$

Now consider like usual a harmonic perturbation of the form $H^{(1)} \propto cos\omega t$. Let's express the perturbation more exactly.

$$H^{(1)} = -\mu \cdot \epsilon = -\mu \cdot \epsilon_0 cos\omega t$$

Take the z component for simplicity like usual.

$$H^{(1)} = -\mu_z\epsilon_0 cos\omega t$$

Evaluate the transition probability now.

$$\begin{aligned}
P_k &= \frac{1}{\hbar^2}\left|\int_{t_0}^{t} dt^{'} e^{i\omega_{kn}t^{'}} < k|H^{(1)}|n >\right|^2 \\
&= \frac{1}{\hbar^2}\left|\int_{t_0}^{t} dt^{'} e^{i\omega_{kn}t^{'}} < k| - \mu_z \epsilon_0 cos\omega t^{'}|n >\right|^2 \\
&= \frac{1}{\hbar^2}\left|\int_{t_0}^{t} dt^{'} e^{i\omega_{kn}t^{'}} (-\epsilon_0) cos\omega t^{'} < k|\mu_z|n >\right|^2 \\
&= \frac{\epsilon_0^2| < k|\mu_z|n > |^2}{\hbar^2}\left|\int_{t_0}^{t} dt^{'} e^{i\omega_{kn}t^{'}} \left(\frac{e^{i\omega t^{'}} + e^{-i\omega t^{'}}}{2}\right)\right|^2 \\
&= \frac{\epsilon_0^2| < k|\mu_z|n > |^2}{4\hbar^2}\left|\int_{t_0}^{t} dt^{'} e^{i(\omega_{kn}+\omega)t^{'}} + e^{i(\omega_{kn}-\omega)t^{'}}\right|^2
\end{aligned}$$

Let's consider the last term separately for convenience.

$$= \frac{(e^{i(\omega_{kn}+\omega)t} - e^{i(\omega_{kn}+\omega)t_0})}{i(\omega_{kn}+\omega)} + \frac{e^{i(\omega_{kn}-\omega)t} - e^{i(\omega_{kn}-\omega)t_0}}{i(\omega_{kn}-\omega)}$$

Let $t_0 = 0$ for convenience

$$= \frac{(e^{i(\omega_{kn}+\omega)t} - 1)}{i(\omega_{kn}+\omega)} + \frac{(e^{i(\omega_{kn}-\omega)t} - 1)}{i(\omega_{kn}-\omega)}$$

Now take the Rotating wave approximation and drop the 1st term.

$$= \frac{(e^{i(\omega_{kn}-\omega)t} - 1)}{i(\omega_{kn}-\omega)}$$

Now extract out $e^{\frac{i(\omega_{kn}-\omega)t}{2}}$ to get

$$\begin{aligned}
&= \frac{e^{\frac{i(\omega_{kn}-\omega)t}{2}}}{(\omega_{kn}-\omega)}\left(\frac{e^{\frac{i(\omega_{kn}-\omega)t}{2}} - e^{\frac{-i(\omega_{kn}-\omega)t}{2}}}{i}\right) \\
&= 2e^{\frac{i(\omega_{kn}-\omega)t}{(\omega_{kn}-\omega)}}\left(\frac{e^{i(\omega_{kn}-\omega)t} - e^{-i(\omega_{kn}-\omega)t}}{2i}\right) \\
&= 2e^{\frac{i(\omega_{kn}-\omega)t}{(\omega_{kn}-\omega)}} sin\frac{(\omega_{kn}-\omega)t}{2}
\end{aligned}$$

Now square the term and replace back into our original expression.

$$P_k = \frac{\epsilon_0^2| < k|\mu_z|n > |^2}{4\hbar^2}\frac{4sin^2\frac{\omega_{kn}-\omega t}{2}}{(\omega_{kn}-\omega)^2}$$

$$\boxed{P_k = \frac{\epsilon_0^2|<k|\mu_z|n>|^2}{\hbar^2}\frac{sin^2\frac{(\omega_{kn}-\omega)t}{2}}{(\omega_{kn}-\omega)^2}} \tag{28.7}$$

Desired expression for transition probability with a harmonic (cosine) perturbation. It is identical to our previous transition probability derived using a harmonic (sine) perturbation. Makes no difference.

Summary

$$\boxed{P_{k,\text{constant}} = \frac{4|<k|H^{(1)}|n>|^2}{\hbar^2}\left(\frac{sin^2\frac{\omega_{kn}t}{2}}{\omega_{kn}^2}\right)} \tag{28.8}$$

$$\boxed{P_{k,\text{harmonic, sin}} = \frac{\epsilon_0^2|<k|\mu_z|n>|^2}{\hbar^2}\left(\frac{sin^2\frac{(\omega_{kn}-\omega)t}{2}}{(\omega_{kn}-\omega)^2}\right)} \tag{28.9}$$

$$\boxed{P_{k,\text{harmonic, cos}} = \frac{\epsilon_0^2|<k|\mu_z|n>|^2}{\hbar^2}\left(\frac{sin^2\frac{(\omega_{kn}-\omega)t}{2}}{(\omega_{kn}-\omega)^2}\right)} \tag{28.10}$$

Extension

However, these expressions can be re-expressed in the limit where $t \to \infty$ (as some authors do by invoking an alternative definition of the Delta function. This is because as t increases the peak in the above expressions becomes narrower and taller approaching a Delta function at infinitely long times.)

$$\boxed{\delta(x) = lim_{a\to\infty}\frac{sin^2(ax)}{\pi a x^2}} \tag{28.11}$$

$H^{(1)}constant$

So looking above $t \to \infty$ and $x \to \frac{\omega_{kn}}{2}$

$$\delta(\frac{\omega_{kn}}{2}) = lim_{t\to\infty}\frac{sin^2\frac{t\omega_{kn}}{2}}{\pi t(\frac{\omega_{kn}}{2})^2}$$

$$\begin{aligned} P_{k-H^{(1)}constant} &= \frac{|<k|H^{(1)}|n>|^2}{\hbar^2}\left(\frac{sin^2\frac{\omega_{kn}t}{2}}{\pi t(\frac{\omega_{kn}}{2})^2}\right)\pi t \\ &= \frac{\pi|<k|H^{(1)}|n>|^2}{\hbar^2}\delta(\frac{\omega_k-\omega_n}{2})t \end{aligned}$$

Convert the $\delta(\omega_k - \omega_n)$ term to $\delta(\epsilon_k - \epsilon_n)$. Note that

$$\delta\left(\frac{\omega_k - \omega_n}{2}\right) = 2\hbar\delta(\epsilon_k - \epsilon_n)$$

We get

$$\boxed{P_{k-H^{(1)}constant} = \frac{2\pi}{\hbar}| < k|H^{(1)}|n > |^2\delta(\epsilon_k - \epsilon_n)t} \qquad (28.12)$$

This is the $t \rightarrow \infty$ expression for the transition probability for constant $H^{(1)}$.

The rate is

$$\boxed{R = \frac{dP_k}{dt} = \frac{2\pi}{\hbar}| < k|H^{(1)}|n > |^2\delta(\epsilon_k - \epsilon_n)} \qquad (28.13)$$

This is the desired transition rate in the $t \rightarrow \infty$ limit (the long time limit). It is also sometimes referred to as Fermi's Golden rule by some people.

$H^{(1)}$ harmonic (sine or cosine)

Looking above as $a \rightarrow t$ and $x \rightarrow \frac{(\omega_{kn}-\omega)}{2}$ we get

$$\delta(\frac{\omega_{kn} - \omega}{2}) = lim_{t\rightarrow\infty}\frac{sin^2(t\frac{\omega_{kn}-\omega}{2})}{\pi t(\frac{\omega_{kn}-\omega}{2})^2}$$

$$\begin{aligned} P_{k-harmonic} &= \frac{\epsilon_0^2| < k|\mu_z|n > |^2}{4\hbar^2}\frac{sin^2\frac{(\omega_{kn}-\omega)t}{2}\pi t}{\pi t\left(\frac{(\omega_{kn}-\omega)}{4}\right)} \\ &= \frac{\pi\epsilon_0^2}{4\hbar^2}| < k|\mu_z|n > |^2\delta(\frac{\omega_{kn} - \omega}{2})t \end{aligned}$$

where

$$\delta(\frac{\omega_{kn} - \omega}{2}) = \delta(\frac{\omega_k - \omega_n - \omega}{2}) = 2\hbar\delta(\epsilon_k - \epsilon_n - \epsilon)$$

$$\boxed{\delta(\frac{\omega_{kn}-\omega}{2}) = 2\hbar\delta(\epsilon_k - \epsilon_n - \epsilon)} \qquad (28.14)$$

leaving

$$\begin{aligned} P_{k-harmonic} &= \frac{\pi\epsilon_0^2(2\hbar)}{4\hbar^2}| < k|\mu_z|n > |^2\delta(\epsilon_k - \epsilon_n - \epsilon)t \\ &= \frac{2\pi}{\hbar}\left(\frac{\epsilon_o^2}{4}\right)| < k|\mu_z|n > |^2\delta(\epsilon_k - \epsilon_n - \epsilon)t \end{aligned}$$

or finally

$$\boxed{P_{k-harmonic} = \tfrac{\pi\epsilon_0^2}{2\hbar}| < k|\mu_z|n > |^2\delta(\epsilon_k - \epsilon_n - \epsilon)} \tag{28.15}$$

This is the desired transition probability in the $t \to \infty$ limit for a harmonic perturbation.

The rate is

$$\boxed{R = \tfrac{dP_k}{dt} = \tfrac{\pi\epsilon_0^2}{2\hbar}| < k|\mu_z|n > |^2\delta(\epsilon_k - \epsilon_n - \epsilon)} \tag{28.16}$$

This is the desired rate in the $t \to \infty$ limit for a harmonic perturbation. (Also called Fermi's Golden rule by some.) Alternatively one can write

$$R = \frac{2\pi}{\hbar}\left(\frac{\epsilon_o^2}{4}\right) | < k|\mu_z|n > |^2\delta(\epsilon_k - \epsilon_n - \epsilon)$$

Chapter 29

Adiabatic perturbations

Now implicit to our previous derivations for either constant time-independent or harmonic perturbations was the assumption that the perturbation was turned on sharply at $t = t_0$ or $t = 0$ if you will.

In many cases, the potential actually turns on more slowly.

So what happens to our derived expressions if the perturbation is turned on slowly. Do they change?

Constant time-independent perturbation, adiabatic approximation

Assume

$$H^{(1)}(t) = e^{\eta t} H^{(1)}$$

Note that $H^{(1)}$ is our time independent perturbation from before where $\eta > 0$ and $\eta \to 0$ slowly. We calculate the transition probability using this slow turn on representation.

$$\begin{aligned}
P_k &= \frac{1}{\hbar^2} \left| \int_{t_0}^{t} dt^{'} e^{i\omega_{kn} t^{'}} < k|H^{(1)}(t)|n > \right|^2 \\
&= \frac{1}{\hbar^2} \left| \int_{t_0}^{t} dt^{'} e^{i\omega_{kn} t^{'}} < k|e^{\eta t^{'}} H^{(1)}|n > \right|^2 \\
&= \frac{1}{\hbar^2} \left| \int_{t_0}^{t} dt^{'} e^{i\omega_{kn} t^{'}} e^{\eta t^{'}} < k|H^{(1)}|n > \right|^2 \\
&= \frac{| < k|H^{(1)}|n > |^2}{\hbar^2} \left| \int_{t_0}^{t} dt^{'} e^{(i\omega_{kn} + \eta)t^{'}} \right|^2
\end{aligned}$$

Evaluate the integral separately for convenience and for sake of simplicity let $t_0 \to -\infty$. In this limit the contribution of $e^{\eta t_0}$ is very small and can be ignored.

$$\begin{aligned} &= \frac{(e^{(i\omega_{kn}+\eta)t} - e^{i\omega_{kn}+\eta})t_0}{(i\omega_{kn}+\eta)} \\ &\simeq \frac{e^{(i\omega_{kn}+\eta)t}}{(i\omega_{kn}+\eta)} \end{aligned}$$

Now square the term and replace it back within our original expression.

$$\boxed{P_k = \tfrac{|<k|H^{(1)}|n>|^2}{\hbar^2}\left(\tfrac{e^{2\eta t}}{\omega_{kn}^2+\eta^2}\right)} \tag{29.1}$$

This is the desired transition probability.

Now for the rate

$$\begin{aligned} R = \frac{dP_k}{dt} &= \frac{|<k|H^{(1)}|n>|^2}{\hbar^2}\frac{(2\eta e^{2\eta t})}{(\omega_{kn}^2+\eta^2)} \\ &= \frac{|<k|H^{(1)}|n>|^2}{\hbar^2}\frac{2\eta e^{2\eta t}}{(\omega_{kn}^2+\eta^2)} \end{aligned}$$

Let $\eta \to 0$ (arbitarily slow turn on)

$$R = \frac{|<k|H^{(1)}|n>|^2}{\hbar^2}\frac{2\eta}{(\omega_{kn}^2+\eta^2)}$$

since $e^{2\eta t} \to 1$ very fast.

$$R = \frac{2|<k|H^{(1)}|n>|^2}{\hbar^2}\frac{\eta}{(\omega_{kn}^2+\eta^2)}$$

Now note that another expression for the Delta function goes as (who knew there were so many definitions)

$$\boxed{\delta(x) = lim_{\epsilon\to 0}\tfrac{1}{\pi}\left(\tfrac{\epsilon}{x^2+\epsilon^2}\right)} \tag{29.2}$$

So by comparison with our expression $\eta \to \epsilon$ and $x \to \omega_{kn}$

$$lim_{\eta\to 0}\frac{\eta}{\omega_{kn}^2+\eta^2} = \pi\delta(\omega_{kn})$$

We now have

$$R = \frac{2| < k|H^{(1)}|n > |^2}{\hbar^2}\pi\delta(\omega_{kn})$$

where $\delta(\omega_{kn}) = \delta(\omega_k - \omega_n)$ and $\delta(\epsilon_k - \epsilon_n) = \frac{\delta(\omega_k - \omega_n)}{\hbar}$ since by definition of the delta function $\delta(cx) = \frac{1}{c}\delta(x)$

$$R = \frac{2\pi}{\hbar^2}| < k|H^{(1)}|n > |^2\hbar\delta(\epsilon_k - \epsilon_n)$$

Our desired transition rate in the adiabatic limit for a time independent perturbation is therefore

$$\boxed{\frac{2\pi}{\hbar}| < k|H^{(1)}|n > |^2\delta(\epsilon_k - \epsilon_n)} \tag{29.3}$$

You can see that this expression is identical to that derived earlier. So the expression is insensitive to how fast the perturbation was turned on. (Fermi's Golden rule does not change)

Time-independent harmonic perturbation, adiabatic approximation

Ok, let's do the harmonic perturbation counterpart in the adiabatic (slow turn on) limit. Do we expect the final expression to change?

Assume $H^{(1)}(t) = e^{\eta t}(-\mu \cdot \epsilon)$

$$H^{(1)}(t) = -e^{\eta t}\mu_z\epsilon_0 cos\omega t$$

where we took the z component for simplicity like usual.

$$\boxed{H^{(1)} = -e^{\eta t}\mu_z\epsilon_0 cos\omega t} \tag{29.4}$$

Gradually turn on the perturbation through η and eventually let $\eta \rightarrow 0$

at the end of the problem. The transition probability we want is

$$\begin{aligned}
P_k &= \frac{1}{\hbar^2}\left|\int_{t_0}^{t} dt^{'}\, e^{i\omega_{kn}t^{'}} < k|H^{(1)}|n>\right|^2 \\
&= \frac{1}{\hbar^2}\left|\int_{t_0}^{t} dt^{'}\, e^{i\omega_{kn}t^{'}} < k| - e^{\eta t^{'}}\mu_z\epsilon_0 cos\omega t^{'}|n>\right|^2 \\
&= \frac{1}{\hbar^2}\left|\int_{t_0}^{t} dt^{'}\, e^{i\omega_{kn}t^{'}} e^{\eta t^{'}} cos\omega t^{'}\epsilon_0 < k|\mu_z|n>\right|^2 \\
&= \frac{\epsilon_0^2|<k|\mu_z|n>|^2}{\hbar^2}\left|\int_{t_0}^{t} dt^{'}\, e^{(i\omega_{kn}+\eta)t^{'}} cos\omega t^{'}\right|^2 \\
&= \frac{\epsilon_0^2|<k|\mu_z|n>|^2}{\hbar^2}\left|\int_{t_0}^{t} dt^{'}\, e^{(i\omega_{kn}+\eta)t^{'}} \frac{e^{i\omega t^{'}} + e^{-i\omega t^{'}}}{2}\right|^2 \\
&= \frac{\epsilon_0^2|<k|\mu_z|n>|^2}{4\hbar^2}\left|\int_{t_0}^{t} dt^{'}\, e^{(i\omega_{kn}+\eta+i\omega)t^{'}} + e^{(i\omega_{kn}+\eta-i\omega)t^{'}}\right|^2 \\
&= \frac{\epsilon_0^2|<k|\mu_z|n>|^2}{4\hbar^2}\left|\int_{t_0}^{t} dt^{'}\, e^{[i(\omega_{kn}+\omega)+\eta]t^{'}} + e^{[i(\omega_{kn}-\omega)+\eta]t^{'}}\right|^2
\end{aligned}$$

Consider the integral separately for convenience.

$$= \frac{(e^{[i(\omega_{kn}+\omega)+\eta]t} - e^{[i(\omega_{kn}+\omega)+\eta]t_0})}{[i(\omega_{kn}+\omega)+\eta]} + \frac{(e^{[i(\omega_{kn}-\omega)+\eta]t} - e^{[i(\omega_{kn}-\omega)+\eta]t_0})}{[i(\omega_{kn}-\omega)+\eta]}$$

Like usual invoke the Rotating Wave approximation and keep only the term strongest near resonance (drop the 1st term) leaving

$$= \frac{(e^{[i(\omega_{kn}-\omega)+\eta]t} - e^{[i(\omega_{kn}-\omega)+\eta]t_0})}{[i(\omega_{kn}-\omega)+\eta]}$$

Now like before let $t_0 \to -\infty$ and note that $e^{\eta t}$ has negligible contribution here so that this term approaches zero and can be dropped.

$$\simeq \frac{e^{[i(\omega_{kn}-\omega)+\eta]t}}{[i(\omega_{kn}-\omega)+\eta]}$$

Now take the square of this term and replace it back into our original expression.

$$\boxed{P_k = \frac{\epsilon_0|<k|\mu_z|n>|^2}{4\hbar^2}\frac{e^{2\eta t}}{[(\omega_{kn}-\omega)^2+\eta^2]}} \tag{29.5}$$

Desired expression for the transition probablity.

Now find the rate $R = \frac{dP_k}{dt}$

$$\begin{aligned} R &= \frac{\epsilon_0^2| < k|\mu_z|n > |^2}{4\hbar^2} \frac{2\eta e^{2\eta t}}{[(\omega_{kn} - \omega)^2 + \eta^2]} \\ &= \frac{\epsilon_0^2| < k|\mu_z|n > |^2}{2\hbar^2} \frac{\eta e^{2\eta t}}{[(\omega_{kn} - \omega)^2 + \eta^2]} \end{aligned}$$

Now like before let $\eta \to 0$

$$R = \frac{\epsilon_0^2| < k|\mu_z|n > |^2}{2\hbar^2} \frac{\eta}{[(\omega_{kn} - \omega)^2 + \eta^2]}$$

because $e^{2\eta t} \to 0$ quickly as $y \to 0$.

Now recognize like before that the delta function is defined in many ways and that

$$\delta(x) = lim_{\epsilon \to 0} \frac{1}{\pi} (\frac{\epsilon}{x^2 + \epsilon^2})$$

so by comparison $\epsilon \to \eta$ and $x \to (\omega_{kn} - \omega)$.

$$lim_{\eta \to 0} \frac{\eta}{(\omega_{kn}^2 + \eta^2)^2 + \eta^2} = \pi \delta(\omega_{kn} - \omega)$$

$$R = \frac{\epsilon_0 \pi| < k|\mu_z|n > |^2}{2\hbar^2} \delta(\omega_{kn} - \omega)$$

Now convert $\delta(\omega_{kn} - \omega) = \delta(\omega_k - \omega_n - \omega) \to \delta(\epsilon_k - \epsilon_n - \epsilon)$ where

$$\delta(\omega_k - \omega_n - \omega) = \hbar \delta(\epsilon_k - \epsilon_n - \epsilon)$$

since by definition $\delta(cx) = \frac{1}{c}\delta(x)$.

The rate is therefore

$$\boxed{R = \frac{\pi\epsilon_0^2|<k|\mu_z|n>|^2}{2\hbar} \delta(\epsilon_k - \epsilon_n - \epsilon)} \qquad (29.6)$$

This is our desired transition rate in the adiabatic limit for a harmonic perturbation. Note again that it is exactly identical to our previously derived expression. So it is insensitive to how fast the perturbation was turned on. Also this is referred to as Fermi's Golden rule by some. You can see that it is again insensitive to how fast or slow the perturbation was turned on.

Chapter 30

Fermi's Golden Rule

A lot of the nuts and bolts of we've done before. Here we will derive from the transition probability P_k the transition rate through $R = \frac{dP_k}{dt}$ and then consider not necessarily one state but a spread or a distribution of final states. Then we will call this result, Fermi's Golden Rule.

Rather than start from scratch and re-derive the trnasition probabilities we will use our results previously derived for 2 general cases

- $H^{(1)}$ is constant and independent of time
- $H^{(1)}$ is harmonic (sine or cosine)

$H^{(1)}$ constant, time independent

Start with the derived transition probability

$$\boxed{P_k = \frac{4|<k|H^{(1)}|n>|^2}{\hbar^2}\frac{sin^2\frac{\omega_{kn}t}{2}}{\omega_{kn}^2}} \tag{30.1}$$

Note that $\omega_{kn} = (\omega_k - \omega_n)$ where k is the final state and n is the initial state.

Now assume a spread of final states k where the density of final states is $\rho(\epsilon_k)$ or $\rho(\omega_k)$.

To accurately consider the contribution from each state k in the distribution we must integrate the above P_k over the spread of final states to get $P_{k,group}$.

As an aside, the number of states with ϵ_k or ω_k between ϵ_k and $\epsilon_k + d\epsilon_k$ or ω_k and $d\omega_k$ is $\rho(\epsilon_k)d\epsilon_k$ or $\rho(\omega_k)d\omega_k$. We have

$$\boxed{P_{k,group} = \int_{-\infty}^{\infty} P_k(\omega_k, t)\rho(\omega_k)d\omega_k} \tag{30.2}$$

$$\begin{aligned} P_{k,group} &= \int_{-\infty}^{\infty} \frac{4|<k|H^{(1)}|n>|^2}{\hbar^2}\left(\frac{sin^2\frac{\omega_{kn}t}{2}}{\omega_{kn}^2}\right)\rho(\omega_k)d\omega_k \\ &= \frac{4|<k|H^{(1)}|n>|^2}{\hbar^2}\int_{-\infty}^{\infty}\frac{sin^2\frac{\omega_{kn}t}{2}}{\omega_{kn}^2}\rho(\omega_k)d\omega_k \\ &= \frac{4|<k|H^{(1)}|n>|^2}{\hbar^2}\int_{-\infty}^{\infty}\frac{sin^2\frac{(\omega_k-\omega_n)t}{2}}{(\omega_k-\omega_n)^2}\rho(\omega_k)d\omega_k \end{aligned}$$

Now here we generally assume that $\rho(\omega_k)$ is constant (or that the distribution is "uniform"). It can now be removed from the integral. Call it ρ_0

$$= \frac{4|<k|H^{(1)}|n>|^2}{\hbar^2}\rho_0\int_{-\infty}^{\infty}\frac{sin^2\frac{(\omega_k-\omega_n)t}{2}}{(\omega_k-\omega_n)^2}d\omega_k$$

Now let $x = (\omega_k - \omega_n)$ and $dx = d\omega_k$. Also remember to change the limits of integration.

$$= \frac{4|<k|H^{(1)}|n>|^2}{\hbar^2}\rho_0\int_{-\infty}^{\infty}\frac{sin^2\frac{xt}{2}}{x^2}dx$$

From definite integral tables

$$\int_0^{\infty}\frac{sin^2 px}{x^2}dx = \frac{\pi p}{2}$$

Therefore

$$\int_{-\infty}^{\infty}\frac{sin^2 px}{x^2}dx = \pi p$$

where $p = \frac{t}{2}$

We now have

$$\begin{aligned} P_{k,group} &= \frac{4|<k|H^{(1)}|n>|^2}{\hbar^2}\rho_0\frac{\pi t}{2} \\ &= \frac{2\pi|<k|H^{(1)}|n>|^2\rho_0 t}{\hbar^2} \end{aligned}$$

Our desired transition probability into a group of final states is

$$\boxed{P_{k,group} = \frac{2\pi\rho_o|<k|H^{(1)}|n>|^2 t}{\hbar^2}} \tag{30.3}$$

Now we can get the desired rate

$$\boxed{R = \frac{dP_k}{dt} = \frac{2\pi\rho_o|<k|H^{(1)}|n>|^2}{\hbar^2}} \tag{30.4}$$

Now we could stop here and call this Fermi's Golden rule but typically people will express this in terms of ϵ_k over ω_k. So to be consistent, recognize that $\rho_0 = \rho(\omega_k) = \hbar\rho(\epsilon_k)$ since $\epsilon_k = \hbar\omega_k$. This can be seen from the equality $\int \rho(\omega_k)d\omega_k = \int \rho(\epsilon_k)d\epsilon_k$. However since $\epsilon_k = \hbar\omega_k$ we have $d\epsilon_k = \hbar d\omega_k$ or that $\int \rho(\omega_k)d\omega_k = \int \hbar\rho(\epsilon_k)d\omega_k$. Putting it all together we have $\rho(\omega_k) = \hbar\rho(\epsilon_k)$.

$$\boxed{\tfrac{2\pi}{\hbar}\rho(\epsilon_k)| < k|H^{(1)}|n > |^2} \tag{30.5}$$

You can see that this rate is independent of time and is the quantum mechanical expression of a classical rate for some process.

$H^{(1)}$ harmonic perturbation (sine or cosine)

$$\boxed{H^{(1)} = -\mu_z\epsilon_o cos\omega t} \tag{30.6}$$

$$\boxed{H^{(1)} = -\mu_z\epsilon_o sin\omega t} \tag{30.7}$$

From our previous work we derived

$$P_k = \frac{\epsilon_0^2| < k|\mu_z|n > |^2}{\hbar^2}\frac{sin^2\frac{\omega_{kn}-\omega}{2}t}{(\omega_{kn}-\omega)^2}$$

where again $\omega_{kn} = (\omega_k - \omega_n)$.

Like above, we want to consider the transition probability and more specifically the rate of transition into a group of final states k (not just into one state).

So we integrate over the spread of final states dictated by the density $\rho(\epsilon_k)$ or $\rho(\omega_k)$.

$$\boxed{P_{k,group} = \textstyle\int_{-\infty}^{\infty} P_k(\omega_k, t)\rho(\omega_k)d\omega_k} \tag{30.8}$$

$$\begin{aligned} P_{k,group} &= \int_{-\infty}^{\infty} \frac{\epsilon_0| < k|\mu_z|n > |^2}{\hbar^2}\frac{sin^2\frac{\omega_{kn}-\omega}{2}}{(\omega_{kn}-\omega)^2}\rho(\omega_k)d\omega_k \\ &= \int_{-\infty}^{\infty} \frac{\epsilon_0| < k|\mu_z|n > |^2}{\hbar^2}\frac{sin^2\frac{\omega_k-\omega_n-\omega}{2}}{(\omega_k-\omega_n-\omega)^2}\rho(\omega_k)d\omega_k \end{aligned}$$

Now as before, assume that $\rho(\omega_k)$ is constant or rather that the distribution is uniform. It can be removed from the integral.

$$P_{k,group} = \frac{\epsilon_0^2 \rho(\omega_k) | < k|\mu_z|n > |^2}{\hbar^2} \int_{-\infty}^{\infty} \frac{sin^2 \frac{\omega_k - \omega_n - \omega}{2} t}{(\omega_k - \omega_n - \omega)^2} d\omega_k$$

Let $x = (\omega_k - \omega_n - \omega)$ and $dx = d\omega_k$. Also remember to change the limits of integration. We then get

$$P_{k,group} = \frac{\epsilon_0^2 \rho(\omega_k) | < k|\mu_z|n > |^2}{\hbar^2} \int_{-\infty}^{\infty} \frac{sin^2 \frac{xt}{2}}{x^2} dx$$

As before, from a table of integrals the definite integral is

$$\int_{-\infty}^{\infty} \frac{sin^2 \frac{xt}{2}}{x^2} dx = \frac{\pi t}{2}$$

The resulting transition probability is then

$$P_{k,group} = \frac{\epsilon_0^2 \rho(\omega_k) | < k|\mu_z|n > |^2}{\hbar^2} \frac{\pi t}{2}$$

Also like before, rather than stop here, flip $\rho(\omega_k)$ into $\rho(\epsilon_k)$ to keep the notation consistent with other texts ($\rho(\omega_k) = \hbar \rho(\epsilon_k)$).

$$\boxed{P_{k,group} = \frac{\pi \epsilon_0^2 \rho(\epsilon_k)}{2\hbar} | < k|\mu_z|n > |^2 t} \tag{30.9}$$

This is the desired form of the transition probability.

Now the desired rate is $R = \frac{dP_{k,group}}{dt}$.

$$\boxed{R = \frac{\pi}{2\hbar} \epsilon_0^2 \rho(\epsilon_k) | < k|\mu_z|n > |^2} \tag{30.10}$$

Again, the rate is constant with respect to time. It is the quantum mechanical version of a classical rate. This is called Fermi's Golden Rule.

Chapter 31

Fermi's First Golden Rule

We claim that if there is no direct coupling between an initial state $|n>$ and a final state $|k>$ the transition rate from the intial state to the final state via intermediate states is given by Fermi's 1st Golden Rule.

Recall that to 2nd order, the corrected wavefunctions (or state vectors) in the interaction representation is

$$\begin{aligned} |\Psi_I(t)> &= |\Psi_I(t_0)> + \frac{1}{i\hbar}\int_{t_0}^{t} dt^{'} H^{(1)^{'}} |\Psi_I(t_0)> \\ &+ \frac{1}{(i\hbar)^2}\int_{t_0}^{t} dt^{'} \int_{t_0}^{t^{'}} dt^{''} H^{(1)^{'}}(t^{'}) H^{(1)^{'}}(t^{''}) |\Psi_I(t_0)> \qquad (31.1) \end{aligned}$$

where we will call $|\Psi_I(t_0)>=|n>$ (our usual intial state) and $|\Psi_I(t_0)>=|\Psi_s(t_0)>$.

We want the transition probability and transition rate. To get this we need to first get $C_k =< k|\Psi(t)>$ from which we obtain $P_k = |C_k(t)|^2$ and also $R = \frac{dP_k}{dt}$.

$$\begin{aligned} C_k(t) &= < k| \left[|n> + \frac{1}{i\hbar}\int_{t_0}^{t} dt^{'} H^{(1)^{'}} |n> + \frac{1}{(i\hbar)^2}\int_{t_0}^{t} dt^{'} \int_{t_0}^{t^{'}} dt^{''} H^{(1)^{'}}(t^{'}) H^{(1)^{'}}(t^{''}) |n> \right] \\ &= < k|n> + \frac{1}{i\hbar}\int_{t_0}^{t} dt^{'} < k|H^{(1)^{'}}|n> + \frac{1}{(i\hbar)^2}\int_{t_0}^{t} dt^{'} \int_{t_0}^{t^{'}} dt^{''} < k|H^{(1)^{'}}(t^{'}) H^{(1)^{'}}(t^{''})|n> \\ &= \delta_{kn} + \frac{1}{i\hbar}\int_{t_0}^{t} dt^{'} < k|H^{(1)^{'}}|n> + \frac{1}{(i\hbar)^2}\int_{t_0}^{t} dt^{'} \int_{t_0}^{t^{'}} dt^{''} < k|H^{(1)^{'}}(t^{'}) H^{(1)^{'}}(t^{''})|n> \end{aligned}$$

Obviously the delta function out front is zero and furthermore recall that there is no direct coupling between the initial state and the final state so

$< k|H^{(1)'}|n >= 0$. This kills the first term inside the integral leaving

$$\boxed{C_k(t) = \tfrac{1}{i\hbar}\int_{t_0}^{t} dt' \int_{t_0}^{t'} dt'' < k|H^{(1)'}(t')H^{(1)'}(t'')|n >} \tag{31.2}$$

Now lest square this term to get $P_k(t) = |C_k(t)|^2$

$$\boxed{P_k = \tfrac{1}{\hbar^2}\left|\int_{t_0}^{t} dt' \int_{t_0}^{t'} dt'' < k|H^{(1)'}(t')H^{(1)'}(t'')|n >\right|^2} \tag{31.3}$$

Now to evaluate this we insert the Completeness relation for intermediate states

$$\boxed{\textstyle\sum_m |m >< m| = 1} \tag{31.4}$$

resulting in

$$P_k = \frac{1}{\hbar^4}\left|\sum_{m\neq n}\int_{t_0}^{t} dt' \int_{t_0}^{t'} dt'' < k|H^{(1)'(t')}|m >< m|H^{(1)'}(t'')|n >\right|^2$$

Now start simplifying this expression by recalling that in the interaction representation, we are actually hiding some operators

$$H^{(1)'}(t) = e^{\frac{iH^{(0)}t}{\hbar}} H^{(1)}(t) e^{\frac{-iH^{(0)}t}{\hbar}}$$

$$\begin{aligned}
& P_k = \\
& \frac{1}{\hbar^4}\Bigg|\sum_{m\neq n}\int_{t_0}^{t} dt' \int_{t_0}^{t'} dt'' < k|e^{\frac{iH^{(0)}t'}{\hbar}} H^{(1)}(t') e^{\frac{-iH^{(0)}t'}{\hbar}}|m > \\
& < m|e^{\frac{iH^{(0)}t''}{\hbar}} H^{(1)}(t'') e^{\frac{-iH^{(0)}t''}{\hbar}}|n >\Bigg|^2 \\
= \; & \frac{1}{\hbar^4}\Bigg|\sum_{m\neq n}\int_{t_0}^{t} dt' \int_{t_0}^{t'} dt'' e^{\frac{i\epsilon_k^{(0)}t'}{\hbar}} < k|H^{(1)}(t')|m > e^{\frac{-i\epsilon_m^{(0)}t'}{\hbar}} \\
& e^{\frac{i\epsilon_m^{(0)}t''}{\hbar}} < m|H^{(1)}(t'')|n > e^{\frac{-i\epsilon_n^{(0)}t''}{\hbar}}\Bigg|^2 \\
= \; & \frac{1}{\hbar^4}\Bigg|\sum_{m\neq n}\int_{t_0}^{t} dt' \int_{t_0}^{t'} dt'' e^{\frac{i(\epsilon_k^{(0)}-\epsilon_m^{(0)})t'}{\hbar}} < k|H^{(1)}(t')|m > \\
& e^{\frac{i(\epsilon_m^{(0)}-\epsilon_n^{(0)})t''}{\hbar}} < m|H^{(1)}(t'')|n >\Bigg|^2
\end{aligned}$$

Let's switch to ω_k and ω_m notation to speed things up. From this we know that $\omega_{km} = \frac{\epsilon_k^{(0)} - \epsilon_m^{(0)}}{\hbar}$ and $\omega_{mn} = \frac{\epsilon_m^{(0)} - \epsilon_n^{(0)}}{\hbar}$

$$P_k = \frac{1}{\hbar^4}\left|\sum_{m\neq n}\int_{t_0}^{t} dt^{'}\int_{t_0}^{t^{'}} dt^{''} e^{i\omega_{km}t^{'}} < k|H^{(1)}(t^{'})|m > e^{i\omega_{mn}t^{''}} < m|H^{(1)}(t^{''})|n >\right|^2$$

$$\boxed{P_k = \frac{1}{\hbar^4}\left|\sum_{m\neq n}\int_{t_0}^{t} dt^{'}\int_{t_0}^{t^{'}} dt^{''} e^{i\omega_{km}t^{'}} e^{i\omega_{mn}t^{''}} < k|H^{(1)}(t^{'})|m >< m|H^{(1)}(t^{''})|n >\right|^2} \tag{31.5}$$

This is our desired transition probability in 2nd order.

Now at this point you choose your favorite $H^{(1)}(t)$ perturbation and evaluate. Here $H^{(1)}(t)$ can be time independent like before or harmonic and time dependent.

Example, $H^{(1)}$ time independent

As a specific example, let's assume

$$H^{(1)}(t) = H^{(1)}e^{\eta t}$$

where $H^{(1)}$ is time independent (constant) and η is our adiabatic slow turn on switch.

$$\begin{aligned}
P_k &= \frac{1}{\hbar^4}\left|\sum_{m\neq n}\int_{t_0}^{t} dt^{'}\int_{t_0}^{t^{'}} dt^{''} e^{i\omega_{km}t^{'}} e^{i\omega_{mn}t^{''}} < k|H^{(1)}e^{\eta t^{'}}|m >< m|H^{(1)}e^{\eta t^{''}}|n >\right|^2 \\
&= \frac{1}{\hbar^4}\left|\sum_{m\neq n}\int_{t_0}^{t} dt^{'}\int_{t_0}^{t^{'}} dt^{''} e^{i\omega_{km}t^{'}} e^{i\omega_{mn}t^{''}} e^{\eta t^{'}} e^{\eta t^{''}} < k|H^{(1)}|m >< m|H^{(1)}|n >\right|^2 \\
&= \frac{1}{\hbar^4}\left|\sum_{m\neq n} < k|H^{(1)}|m >< m|H^{(1)}|n > \int_{t_0}^{t} dt^{'}\int_{t_0}^{t^{'}} dt^{''} e^{(i\omega_{km}+\eta)t^{'}} e^{(i\omega_{mn}+\eta)t^{''}}\right|^2
\end{aligned}$$

Now evaluate the first integral over $t^{''}$

$$= \left.\frac{e^{(i\omega_{mn}+\eta)t^{''}}}{(i\omega_{mn}+\eta)}\right|_{t_0}^{t^{'}} = \frac{e^{(i\omega_{mn}+\eta)t^{'}} - e^{(i\omega_{mn}+\eta)t_0}}{(i\omega_{mn}+\eta)}$$

Now like before let $t_0 \to -\infty$ and note that $e^{\eta t_0} \to 0$ quickly so that the second term in the numerator is negligible and can be dropped.

$$= \frac{e^{(i\omega_{mn}+\eta)t'}}{(i\omega_{mn}+\eta)}$$

Replace this back into our original expression

$$\begin{aligned}
P_k &= \frac{1}{\hbar^4}\left|\sum_{m\neq n} < k|H^{(1)}|m >< m|H^{(1)}|n > \int_{t_0}^{t} dt' e^{(i\omega_{km}+\eta)t'} \frac{e^{(i\omega_{mn}+\eta)t'}}{(i\omega_{mn}+\eta)}\right|^2 \\
&= \frac{1}{\hbar^4}\left|\sum_{m\neq n} \frac{< k|H^{(1)}|m >< m|H^{(1)}|n >}{(i\omega_{mn}+\eta)} \int_{t_0}^{t} dt' e^{(i\omega_{km}+\eta+i\omega_{mn}+\eta)t'}\right|^2 \\
&= \frac{1}{\hbar^4}\left|\sum_{m\neq n} \frac{< k|H^{(1)}|m >< m|H^{(1)}|n >}{(i\omega_{mn}+\eta)} \int_{t_0}^{t} dt' e^{[i(\omega_k-\omega_n)+2\eta]t'}\right|^2 \\
&= \frac{1}{\hbar^4}\left|\sum_{m\neq n} \frac{< k|H^{(1)}|m >< m|H^{(1)}|n >}{(i\omega_{mn}+\eta)} \int_{t_0}^{t} dt' e^{(i\omega_{kn}+2\eta)t'}\right|^2
\end{aligned}$$

Now consider the last integral separately for convenience

$$= \frac{e^{(i\omega_{kn}+2\eta)t} - e^{(i\omega_{kn}+2\eta)t_0}}{(i\omega_{kn}+2\eta)}$$

Again, let $t_0 \to -\infty$ and note that $e^{2\eta t_0} \to 0$ quickly, so let the second term in the numerator contributes very little (drop this term).

$$P_k = \frac{1}{\hbar^4}\left|\sum_{m\neq n} \frac{< k|H^{(1)}|m >< m|H^{(1)}|n >}{(i\omega_{mn}+\eta)(i\omega_{kn}+2\eta)} e^{(i\omega_{kn}+2\eta)t}\right|^2$$

Pull out the terms which do not depend on m.

$$P_k = \frac{1}{\hbar^4}\left|\frac{e^{(i\omega_{kn}+2\eta)t}}{(i\omega_{kn}+2\eta)} \sum_{m\neq n} \frac{< k|H^{(1)}|m >< m|H^{(1)}|n >}{(i\omega_{mn}+\eta)}\right|^2$$

$$\boxed{P_k = \frac{e^{4\eta t}}{\hbar^4(\omega_{kn}^2+4\eta^2)}\left|\sum_{m\neq n} \frac{<k|H^{(1)}|m><m|H^{(1)}|n>}{(i\omega_{mn}+\eta)}\right|^2} \tag{31.6}$$

This is our desired transition probability in ω notation.

Alternatively, if you like to express things in terms of ϵ recall that $\epsilon = \hbar\omega$

$$P_k = \frac{e^{4\eta t}}{\hbar^2(\omega_{kn}^2 + 4\eta^2)} \left| \sum_{m \neq n} \frac{< k|H^{(1)}|m >< m|H^{(1)}|n >}{\hbar(i\omega_{mn} + \eta)} \right|^2$$

$$\boxed{\frac{e^{4\eta t}}{[\epsilon_{kn}^2 + (2\hbar\eta)^2]} \left| \sum_{m \neq n} \frac{<k|H^{(1)}|m><m|H^{(1)}|n>}{(i\epsilon_{mn} + \hbar\eta)} \right|^2} \tag{31.7}$$

This is our alternative expression for the transition probability.

Now let's move on to Fermi's 1st Golden rule for expressing the transition rate in second order.

Consider as before a density of final states $\rho(\epsilon_k)$. So as before, we must integrate over this density of final states. Also as before, consider a uniform (or constant) distribution.

$$P_{k,group} = \int_{-\infty}^{\infty} P_k \rho(\epsilon_k) d\epsilon_k$$

$$\begin{aligned} P_{k,group} &= \int_{-\infty}^{\infty} \rho(\epsilon_k) \frac{e^{4\eta t}}{[\epsilon_{kn}^2 + (2\hbar\eta)^2]} \left| \sum_{m \neq n} \frac{< k|H^{(1)}|m >< m|H^{(1)}|n >}{(i\epsilon_{mn} + \hbar\eta)} \right|^2 d\epsilon_k \\ &= \rho(\epsilon_k) \left| \sum_{m \neq n} \frac{< k|H^{(1)}|m >< m|H^{(1)}|n >}{(i\epsilon_{mn} + \hbar\eta)} \right|^2 e^{4\eta t} \int_{-\infty}^{\infty} \frac{d\epsilon_k}{[\epsilon_{kn}^2 + (2\hbar\eta)^2]} \end{aligned}$$

Ok now to do the last integral consider the following

$$\int_{-\infty}^{\infty} \frac{dx}{a^2 + x^2} = \int_{-\infty}^{\infty} \frac{dx}{a^2(1 + (\frac{x}{a})^2)}$$

Let $y = \frac{x}{a}$, $dy = \frac{1}{a}dx$ or $dx = ady$ and note that the limits of integration stay the same

$$\begin{aligned} \int_{-\infty}^{\infty} \frac{ady}{a^2(1 + y^2)} &= \int_{-\infty}^{\infty} \frac{dy}{a(1 + y^2)} \\ &= \frac{1}{a} \int_{-\infty}^{\infty} \frac{dy}{(1 + y^2)} \end{aligned}$$

Now let $y = tan\alpha$ or $dy = \frac{1}{cos^2\alpha}d\alpha$ and also remember to change the limits of integration $y = \infty, \alpha \to \frac{\pi}{2}$ and $y = -\infty, \alpha \to -\frac{\pi}{2}$. We get

$$\begin{aligned}
& \frac{1}{a}\int_{\frac{-\pi}{2}}^{\frac{\pi}{2}} \frac{d\alpha}{cos^2\alpha(1+tan^2\alpha)} \\
= & \frac{a}{a}\int_{\frac{-\pi}{2}}^{\frac{\pi}{2}} \frac{d\alpha}{cos^2\alpha + sin^2\alpha} \\
= & \frac{1}{a}\int_{\frac{-\pi}{2}}^{\frac{\pi}{2}} d\alpha \\
= & \frac{1}{a}\,\alpha|_{\frac{-\pi}{2}}^{\frac{\pi}{2}} \\
= & \frac{\pi}{a}
\end{aligned}$$

where $a = (2\hbar\eta)$. We get

$$\int_{-\infty}^{\infty} \frac{d\epsilon_k}{[\epsilon_{kn}^2 + (2\hbar\eta)^2]} = \frac{\pi}{2\hbar\eta}$$

Therefore

$$\boxed{P_{k,group} = \rho(\epsilon_k)e^{4\eta t}\frac{\pi}{2\hbar\eta}\left|\sum_{m\neq n}\frac{<k|H^{(1)}|m><m|H^{(1)}|n>}{(i\epsilon_{mn}+\hbar\eta)}\right|^2} \tag{31.8}$$

This is our desired transition probability in second order into a group of final states.

Now we can get the transition rate in the usual way.

$$\begin{aligned}
R &= \frac{dP_{k,group}}{dt} \\
&= \frac{\rho(\epsilon_k)4\eta e^{4\eta t}\pi}{2\hbar\eta}\left|\sum_{m\neq n}\frac{< k|H^{(1)}|m >< m|H^{(1)}|n >}{(i\epsilon_{mn}+\hbar\eta)}\right|^2 \\
&= \frac{2\pi}{\hbar}e^{4\eta t}\rho(\epsilon_k)\left|\sum_{m\neq n}\frac{< k|H^{(1)}|m >< m|H^{(1)}|n >}{(i\epsilon_{mn}+\hbar\eta)}\right|^2
\end{aligned}$$

Now let $\eta \to 0$ like usual

$$\boxed{R = \frac{2\pi}{\hbar}\rho(\epsilon_k)\left|\sum_{m\neq n}\frac{<k|H^{(1)}|m><m|H^{(1)}|n>}{(i\epsilon_{mn}+\hbar\eta)}\right|^2} \tag{31.9}$$

This is our desired transition rate in second order. This is also Fermi's 1st Golden Rule for the rate of a 2 step process.

Chapter 32

Line Broadening (lifetime broadening)

In the interaction representation we have the wavefunction to 1st order

$$|\Psi_I(t)>=|\Psi_I(t_0)>+\frac{1}{i\hbar}\int_{t_0}^{t}dt^{'}H^{(1)'}(t)|\Psi_I(t_0)>$$

where again recall the prime over $H^{(1)'}$ means that $H^{(1)'}(t)=e^{\frac{iH^{(0)}t}{\hbar}}H^{(1)}(t)e^{\frac{-iH^{(0)}t}{\hbar}}$ and also that $|\Psi_I(t_0)>=|\Psi_s(t_0)>$ in the Schrodinger representation.

Now consider populating a final state k where heuristically that state happens to decay exponentially. Let's also say that the perturbation is harmonic $H^{(1)}\propto sin\omega t$.

Ok so basically our task is to find P_k and see what the exponential decay does.

$$C_k=<k|\Psi_n(t)>$$

where $|\Psi_n(t)>=|n>+\frac{1}{i\hbar}\int_{t_0}^{t}dt^{'}H^{(1)'}(t)|n>$ and where $H^{(1)}(t)=-\mu\cdot\epsilon_0 sin\omega t$. Take the z component for convenience like usual. $H^{(1)}(t)=-\mu_z\epsilon_0 sin\omega t$. Note that this is in the Schrodinger representation.

Ok, here we go

$$\begin{aligned}
C_k &= <k|\left[|n> + \frac{1}{i\hbar}\int_{t_0}^{t} dt' H^{(1)'}(t)|n>\right] \\
&= <k|n> + \frac{1}{i\hbar}\int_{t_0}^{t} dt' <k|H^{(1)'}(t)|n> \\
&= \delta_{kn} + \frac{1}{i\hbar}\int_{t_0}^{t} dt' <k|e^{\frac{iH^{(0)}t'}{\hbar}} H^{(1)}(t) e^{\frac{-iH^{(0)}t'}{\hbar}}|n> \\
&= \frac{1}{i\hbar}\int_{t_0}^{t} dt' e^{\frac{i\epsilon_k^{(0)}t'}{\hbar}} <k|H^{(1)}(t)|n> e^{\frac{-i\epsilon_n^{(0)}t'}{\hbar}} \\
&= \frac{1}{i\hbar}\int_{t_0}^{t} dt' e^{\frac{i(\epsilon_k^{(0)}-\epsilon_n^{(0)})t'}{\hbar}} <k|H^{(1)}(t)|n>
\end{aligned}$$

where $\omega_{kn} = \frac{\epsilon_k - \epsilon_n}{\hbar}$

$$\begin{aligned}
C_k &= \frac{1}{i\hbar}\int_{t_0}^{t} dt' e^{i\omega_{kn}t'} <k|H^{(1)}(t)|n> \\
&= \frac{1}{i\hbar}\int_{t_0}^{t} dt' e^{i\omega_{kn}t'} <k| - \mu_z\epsilon_0 sin\omega t'|n> \\
&= -\frac{\epsilon_0}{i\hbar}\int_{t_0}^{t} dt' e^{i\omega_{kn}t'} sin\omega t <k|\mu_z|n> \\
&= -\frac{\epsilon_0 <k|\mu_z|n>}{i\hbar}\int_{t_0}^{t} dt' e^{i\omega_{kn}t'} \frac{e^{i\omega t'} - e^{-i\omega t'}}{2i} \\
&= \frac{\epsilon_0 <k|\mu_z|n>}{2\hbar}\int_{t_0}^{t} e^{i(\omega_{kn}+\omega)t'} - e^{i(\omega_{kn}-\omega)t'}
\end{aligned}$$

Let's look ahead and recall that there are 2 terms in the integral. One dominates near reasonance and we usually drop the other one. (This is our Rotating Wave approximation). So let's do it.

$$C_k = -\frac{\epsilon_0 <k|\mu_z|n>}{2\hbar}\int_{t_0}^{t} dt' e^{i(\omega_{kn}-\omega)t'}$$

At this point take the derivative of the above expression rather than integrating and evaluating like usual.

$$\frac{dC_k}{dt} = -\frac{\epsilon_0 <k|\mu_z|n>}{2\hbar} e^{i(\omega_{kn}-\omega)t}$$

Now you'll notice that there are no decays in the above expression. The $e^{i(\omega_{kn}-\omega)t}$ term just oscillates. So since we expect the final state to eventually decay at long enough times add such a decay term heuristically to the above expression.

Since in the long time limit $P_k = |C_k|^2 \propto e^{-\Gamma t}$ (exponential decay with some rate Γ) $C_k(t) = e^{\frac{-\Gamma t}{2}}$

$$\frac{dC_k(t)}{dt} = -\frac{\Gamma}{2}e^{\frac{-\Gamma t}{2}} = -\frac{\Gamma}{2}C_k(t)$$

We can add this expression back into our original equation.

$$\frac{dC_k}{dt} = -\frac{\epsilon_0 < k|\mu_z|n >}{2\hbar}e^{i(\omega_{kn}-\omega)t} - \frac{\Gamma}{2}C_k$$

Now the general solution to the 1st order differential equation of the form

$$y^{'} + ay = be^{i\alpha t}$$

is

$$y = Ae^{-at} + \frac{be^{i\alpha t}}{a + i\alpha}$$

So by inspection to our expression

$$C_k(t) = Ae^{\frac{-\Gamma t}{2}}\frac{-\left(\frac{\epsilon_0<k|\mu_z|n>}{2\hbar}\right)}{\frac{\Gamma}{2} + i(\omega_{kn} - \omega)}e^{i(\omega_{kn}-\omega)t}$$

Rearranging gives

$$C_k(t) = Ae^{\frac{-\Gamma t}{2}} - \frac{\epsilon_0 < k|\mu_z|n >}{2\hbar}\frac{e^{i(\omega_{kn}-\omega)t}}{[\frac{\Gamma}{2} + i(\omega_{kn} - \omega)]}$$

At long times one can neglect the first term of the expression.

$$C_k(t) \simeq -\frac{\epsilon_0 < k|\mu_z|n >}{2\hbar}\frac{e^{i(\omega_{kn}-\omega)t}}{[\frac{\Gamma}{2} + i(\omega_{kn} - \omega)]}$$

Finally $P_k = |C_k(t)|^2$

$$\boxed{P_k = \frac{\epsilon_0^2<k|\mu_z|n>}{4\hbar^2}\left(\frac{1}{(\omega_{kn}-\omega)+\frac{\Gamma^2}{4}}\right)} \tag{32.1}$$

This P_k then has a Lorentzian lineshape which is broadened by the exponential decay rate Γ. (This is referred to as lifetime broadening because the state's intrinsic lifetime causes some fatness or natural width to the lineshape. It is an example of homogeneous broadening.)

Chapter 33

Irreversible decay, Fourier transform approach

We want to see how an initially prepared state will decay. Previously we simply asserted that the decay of a state will go exponentially as $\propto e^{-\Gamma t}$. But here we try to prove this assertion.

We will have a final state (or states) called k and an initial state which we will call n. Our goal is to derive how n decays and to show that it will look exponential. Assume a constant time independent perturbation $H^{(1)}$. Also start with the time dependent Schrodinger equation expressed in the interaction representation. Recall that

$$i\hbar \frac{d|\Psi_I(t)>}{dt} = H^{(1)'}(t)|\Psi_I(t)>$$

where in general $|\Psi_I(t)>$ can be expressed as a linear combination of $t = 0$ wavefunctions with time dependent coefficients.

$$|\Psi_I(t)>= \sum_l C_l(t)|l_I>$$

Note at $t = 0$ $|l>_I = |l>_s$. The Schrodinger and interaction wavefunctions are identical. We will drop the I subscript for notational simplicity.

Now since we have an initial state n, $C_n \simeq 1$ but not necessarily identical to 1 and $C_{l\neq n} \simeq 0$.

$$|\Psi_I(t)>= C_n|n>$$

$$i\hbar \frac{d(C_n|n>)}{dt} = H^{(1)'}C_n|n>$$

Multiply through both sides by $< k|$ to isolate an expression for C_k.

$$\begin{aligned} i\hbar\frac{d}{dt}(C_n < k|n >) &= C_n < k|H^{(1)'}|n > \\ i\hbar\frac{dC_k}{dt} &= C_n < k|H^{(1)'}|n > \end{aligned}$$

Now recall that in the interaction representation

$$H^{(1)'} = e^{\frac{iH^{(0)}t}{\hbar}} H^{(1)} e^{\frac{-iH^{(0)}t}{\hbar}}$$

where $H^{(1)}$ is a constant.

$$\begin{aligned} i\hbar\frac{dC_k}{dt} &= C_n < k|e^{\frac{iH^{(0)}t}{\hbar}} H^{(1)} e^{\frac{-iH^{(0)}t}{\hbar}}|n > \\ &= C_n e^{\frac{i\epsilon_k^{(0)}t}{\hbar}} < k|H^{(1)}|n > e^{\frac{-i\epsilon_n^{(0)}t}{\hbar}} \\ &= C_n e^{\frac{i(\epsilon_k^{(0)}-\epsilon_n^{(0)})t}{\hbar}} < k|H^{(1)}|n > \end{aligned}$$

$$\boxed{i\hbar\frac{dC_k}{dt} = C_n e^{i\omega_{kn}t} < k|H^{(1)}|n >} \tag{33.1}$$

where $\omega_{kn} = \frac{\epsilon_k^{(0)}-\epsilon_n^{(0)}}{\hbar}$

$$\frac{dC_k}{dt} = \frac{1}{i\hbar} C_n e^{i\omega_{kn}t} < k|H^{(1)}|n >$$

Integrate to get

$$C_k = \frac{1}{i\hbar}\int_{t_0}^{t} dt' C_n(t') e^{i\omega_{kn}t'} < k|H^{(1)}|n >$$

Also note that we implicitly assume $C_k(0) = 0$ which is reasonable.

At this point physically you have a state n feeding state or states k so here is depletion of the initial n population. But by the same token k can feed n (called feedback) so we can in principle build back population in n. However, it will turn out that this feedback is not perfect and that in the end n basically decays.

$$i\hbar\frac{d}{dt}|\Psi_I(t) >= H^{(1)'}|\Psi_I(t) >$$

where $|\Psi_i(t) >$ is our prepared k state.

$$|\Psi_I(t) >= \sum_k C_k|k >$$

$$i\hbar\frac{d}{dt}\sum_k C_k|k>= H^{(1)'}\sum_k C_k|k>$$

Multiply through by $< n|$ to isolate an expression for C_n

$$< n|\left[i\hbar\frac{d}{dt}\sum_k C_k|k>\right] =< n|H^{(1)'|[\sum_k C_k|k>]}$$

$$\begin{aligned} i\hbar\frac{d}{dt}\sum_k C_k < n|k > &= \sum_k C_k < n|H^{(1)'}|k > \\ i\hbar\frac{dC_n}{dt} &= \sum_k C_k < n|H^{(1)'}|k > \end{aligned}$$

Extract our the possible case where $k = n$ on the right

$$i\hbar\frac{dC_n}{dt} = C_n < n|H^{(1)'}|n > + \sum_{k\neq n} C_k < n|H^{(1)'}|k >$$

Usually the first term on the right hand side is zero but we keep it to stay general.

Now here we take our previously derived expression for C_k and insert it into the above equation.

$$\begin{aligned} i\hbar\frac{dC_n}{dt} &= C_n < n|H^{(1)'}|n > \\ &+ \sum_{k\neq n} < n|H^{(1)'}|k > \left[\frac{1}{i\hbar}\int_{t_0}^{t} dt^{'} C_n(t^{'})e^{i\omega_{kn}t^{'}} < k|H^{(1)}(t^{'})|n >\right] \end{aligned}$$

Convert all $H^{(1)'} \rightarrow H^{(1)}$ where recall that $H^{(1)}$ is constant. We have

$H^{(1)'} = e^{\frac{iH^{(0)}t}{\hbar}} H^{(1)} e^{\frac{-iH^{(0)}t}{\hbar}}$.

$$
\begin{aligned}
i\hbar\frac{dC_n}{dt} &= C_n < n|H^{(1)}|n > \\
&+ \sum_{k\neq n} < n|e^{\frac{iH^{(0)}t}{\hbar}} H^{(1)} e^{\frac{-iH^{(0)}t}{\hbar}}|k > \left[\frac{1}{i\hbar}\int_{t_0}^{t} dt^{'} C_n(t^{'}) e^{i\omega_{kn}t^{'}} < k|H^{(1)}(t^{'})|n >\right] \\
&= C_n < n|H^{(1)}|n > \\
&+ \sum_{k\neq n} e^{-i\omega_{kn}t} < n|H^{(1)}|k > \left[\frac{1}{i\hbar}\int_{t_0}^{t} dt^{'} C_n(t^{'}) e^{i\omega_{kn}t^{'}} < k|H^{(1)}(t^{'})|n >\right] \\
&= \frac{C_n < n|H^{(1)}|n >}{i\hbar} - \frac{1}{\hbar^2}\sum_{k\neq n} e^{-i\omega_{kn}t} < n|H^{(1)}|k > \\
&\int_{t_0}^{t} dt^{'} C_n(t^{'}) e^{i\omega_{kn}t^{'}} < k|H^{(1)}|n > \\
&= \frac{C_n < n|H^{(1)}|n >}{i\hbar} - \frac{1}{\hbar^2}\sum_{k\neq n} | < n|H^{(1)}|k > |^2 e^{-i\omega_{kn}t} \\
&\int_{t_0}^{t} dt^{'} C_n(t^{'}) e^{i\omega_{kn}t^{'}} \\
&= \frac{C_n < n|H^{(1)}|n >}{i\hbar} - \frac{1}{\hbar^2}\sum_{k\neq n} | < n|H^{(1)}|k > |^2 \\
&\int_{t_0}^{t} dt^{'} C_n(t^{'}) e^{i\omega_{kn}t^{'}} e^{-i\omega_{kn}t} \\
&= \frac{C_n < n|H^{(1)}|n >}{i\hbar} - \frac{1}{\hbar^2}\sum_{k\neq n} | < n|H^{(1)}|k > |^2 \int_{t_0}^{t} dt^{'} C_n(t^{'}) e^{i\omega_{kn}(t^{'}-t)}
\end{aligned}
$$

Assume $C_n(t) = 0$ for $t \leq 0$ allowing us to extend $t_0 \rightarrow -\infty$. Also consider long times $t \rightarrow \infty$

$$
\boxed{\frac{dC_n}{dt} = \frac{C_n < n|H^{(1)}|n >}{i\hbar} - \frac{1}{\hbar^2}\sum_{k\neq n} | < n|H^{(1)}|k > |^2 \int_{-\infty}^{\infty} dt^{'} C_n(t^{'}) e^{i\omega_{kn}(t^{'}-t)}} \tag{33.2}
$$

This equation can be solved by using Fourier transforms defined as

$$
\boxed{C_n(t) = \int_{-\infty}^{\infty} f(\omega) e^{-i\omega t} d\omega} \tag{33.3}
$$

with its inverse tranform of

$$\boxed{f(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} C_n(t)e^{i\omega t}dt} \tag{33.4}$$
$$= \frac{1}{2\pi}\int_0^\infty C_n(t)e^{i\omega t}dt$$

since $C_n(t \leq 0) = 0$

Also note that Fourier transforms are written in a number of ways. For example, some people like to see the forward and reverse Fourier transforms in a more symmetric fashion.

$$\boxed{C_n(t) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} f(\omega)e^{-i\omega t}d\omega} \tag{33.5}$$

Forward tranform

$$\boxed{f(\omega) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} C_n(t)e^{i\omega t}d\omega} \tag{33.6}$$

Accompanying reverse tranform

Alternatively they will write it in terms of linear frequency ν rather than ω

$$\boxed{C_n(t) = \int_{-\infty}^{\infty} f(\nu)e^{-i2\pi\nu t}d\nu} \tag{33.7}$$

Forward transform

$$\boxed{f(\nu) = \int_{-\infty}^{\infty} C_n(t)e^{i2\pi\nu t}d\nu} \tag{33.8}$$

Accompanying reverse transform

These expressions are all the same thing. However, we will use the first convention here.

Multiply both sides of our main equation by $e^{i\omega t}$ and integrate from $t = 0$ to $t = \infty$ and assume $C_n(\infty) = 0$

$$\begin{aligned}\int_0^\infty e^{i\omega t}\frac{dC_n}{dt}dt &= \frac{1}{i\hbar} < n|H^{(1)}|n > \int_0^\infty C_n e^{i\omega t}dt \\ &- \frac{1}{\hbar^2}\sum_{k\neq n} | < n|H^{(1)}|k > |^2 \int_0^\infty e^{i\omega t}dt \int_0^\infty dt' C_n(t')e^{i\omega_{kn}(t'-t)}\end{aligned}$$

Let's do the left hand side first. (Integrate by parts)

$$\int_0^\infty e^{i\omega t}\frac{dC_n}{dt}dt = C_n e^{i\omega t}|_0^\infty - \int_0^\infty C_n i\omega e^{i\omega t}dt$$

Let $u = e^{i\omega t}$, $du = i\omega e^{i\omega t}dt$, $dv = \frac{dC_n}{dt}dt$, $v = C_n$. Using this we get

$$\begin{aligned} &= C_n e^{i\omega t}\big|_0^\infty - i\omega \int_0^\infty C_n e^{i\omega t} dt \\ &= -1 - i\omega \int_0^\infty C_n e^{i\omega t} dt \end{aligned}$$

Now this second term turns out to be our Fourier transform.

$$= -1 - i\omega(2\pi f(\omega))$$

The desired left hand side expression is

$$\boxed{-1 - 2\pi i\omega f(\omega)} \tag{33.9}$$

Let's do the first term on the right hand side now.

$$\frac{1}{i\hbar} < n|H^{(1)}|n > \int_0^\infty C_n e^{i\omega t} dt$$

Clearly this is our Fourier transform again

$$\begin{aligned} &\frac{1}{i\hbar} < n|H^{(1)}|n > (2\pi f(\omega)) \\ = \; & -\frac{2\pi i}{\hbar} < n|H^{(1)}|n > f(\omega) \end{aligned}$$

So far we have

$$\begin{aligned} -1 - 2\pi i\omega f(\omega) &= -\frac{2\pi i}{\hbar} < n|H^{(1)}|n > f(\omega) \\ &- \frac{1}{\hbar^2} \sum_{k \neq n} | < n|H^{(1)}|k > |^2 \int_0^\infty e^{i\omega t} dt \int_0^\infty dt' C_n(t') e^{i\omega_{kn}(t'-t)} \end{aligned}$$

Consolidate terms in t and t' by bringing the term with t our of the second integral.

$$\begin{aligned} -1 - 2\pi i\omega f(\omega) &= -\frac{2\pi i}{\hbar} < n|H^{(1)}|n > f(\omega) \\ &- \frac{1}{\hbar^2} \sum_{k \neq n} | < n|H^{(1)}|k > |^2 \int_0^\infty e^{i\omega t} e^{-i\omega_{kn} t} dt \int_0^\infty dt' C_n(t') e^{i\omega_{kn} t'} \end{aligned}$$

For convenience we will swap $\omega_{kn} \to \omega_{nk}(\omega_{kn} = -\omega_{nk})$

$$\begin{aligned} -1 - 2\pi i\omega f(\omega) &= -\frac{2\pi i}{\hbar} < n|H^{(1)}|n > f(\omega) \\ &- \frac{1}{\hbar^2}\sum_{k\neq n} | < n|H^{(1)}|k > |^2 \int_0^\infty e^{i\omega t}e^{i\omega_{kn}t}dt \int_0^\infty dt^{'} C_n(t^{'})e^{-i\omega_{nk}t^{'}} \\ -1 - 2\pi i\omega f(\omega) &= -\frac{2\pi i}{\hbar} < n|H^{(1)}|n > f(\omega) \\ &- \frac{1}{\hbar^2}\sum_{k\neq n} | < n|H^{(1)}|k > |^2 \int_0^\infty e^{i(\omega+\omega_{nk})t}dt \int_0^\infty dt^{'} C_n(t^{'})e^{-i\omega_{nk}t^{'}} \end{aligned}$$

Now we will fudge things a little bit. To render the integral over t convergent we will introduce $e^{-\epsilon t}$ and at the end of the problem let $\epsilon \to 0$

$$\begin{aligned} -1 - 2\pi i\omega f(\omega) &= -\frac{2\pi i}{\hbar} < n|H^{(1)}|n > f(\omega) \\ &- \frac{1}{\hbar^2}\sum_{k\neq n} | < n|H^{(1)}|k > |^2 \int_0^\infty e^{i(\omega+\omega_{nk})t}e^{-\epsilon t}dt \int_0^\infty dt^{'} C_n(t^{'})e^{-i\omega_{nk}t^{'}} \end{aligned}$$

Now we will integrate the 2 back to back integrals. We will integrate them by parts. We have

$$\int_0^\infty e^{i(\omega+\omega_{nk})t-\epsilon t}dt \int_0^\infty dt^{'} C_n(t^{'})e^{-i\omega_{nk}t^{'}}$$

Call the second integral $g(t)$

$$\int_0^\infty e^{i(\omega+\omega_{nk})t-\epsilon t}g(t)dt$$

where $u = g(t)$, $du = C_n(t)e^{-i\omega_{nk}t}dt$, $dv = e^{i(\omega+\omega_{nk})t-\epsilon t}dt$ and $v = \frac{e^{i(\omega+\omega_{nk})t-\epsilon t}}{i(\omega+\omega_{nk})-\epsilon}$. Integration by parts then give us

$$\left.\frac{g(t)e^{i(\omega+\omega_{nk})t-\epsilon t}}{i(\omega+\omega_{nk})\epsilon}\right|_0^\infty - \int_0^\infty \frac{e^{i(\omega+\omega_{nk})t-\epsilon t}}{i(\omega+\omega_{nk})-\epsilon}C_n(t)e^{-i\omega_{nk}t}dt$$

The entire first term is zero leaving us with

$$\int\int = -\int_0^\infty \frac{e^{i(\omega+\omega_{nk})t-\epsilon t}}{i(\omega+\omega_{nk})-\epsilon}C_n(t)e^{-i\omega_{nk}t}dt$$

Assume now that ϵ is small such that $e^{-\epsilon t} \to 1$. We're going to let $\epsilon \to 0$ anyway at the end of the problem.

$$\begin{aligned} = -\int_0^\infty e^{i\omega t} e^{i\omega_{nk}t} e^{\frac{-i\omega_{nk}t}{i(\omega+\omega_{nk})-\epsilon}} C_n(t)dt &= -\int_0^\infty \frac{e^{i\omega}tC_n(t)dt}{i(\omega+\omega_{nk})-\epsilon} \\ &= -\frac{1}{i(\omega+\omega_{nk})-\epsilon}\int_0^\infty e^{i\omega t}C_n(t)dt \end{aligned}$$

It turns out that the last integral is our Fourier transform again $= f(\omega)(2\pi)$. We then get

$$= \frac{-2\pi f(\omega)}{i(\omega+\omega_{nk})-\epsilon}$$

Now replace this into our main expression for the double integral we have just solved. The expression becomes

$$\begin{aligned} -1 - 2\pi i\omega f(\omega) &= -\frac{2\pi i}{\hbar} < n|H^{(1)}|n > f(\omega) \\ &- \frac{1}{\hbar^2}\sum_{k\neq n} | < n|H^{(1)}|k > |^2 \left(-\frac{2\pi f(\omega)}{i(\omega+\omega_{nk})-\epsilon} \right) \\ 1 + 2\pi i\omega f(\omega) &= \frac{2\pi i}{\hbar} < n|H^{(1)}|n > f(\omega) \\ &+ \frac{1}{\hbar^2}\sum_{k\neq n} | < n|H^{(1)}|k > |^2 \left(\frac{-2\pi f(\omega)}{i(\omega+\omega_{nk})-\epsilon} \right) \\ 1 + 2\pi i\omega f(\omega) &= \frac{2\pi i}{\hbar} < n|H^{(1)}|n > f(\omega) \\ &+ \frac{1}{\hbar^2}\sum_{k\neq n} | < n|H^{(1)}|k > |^2 \left(\frac{2\pi f(\omega)}{-i(\omega+\omega_{nk})+\epsilon} \right) \end{aligned}$$

Now an important approximation here is to let $\omega = 0$ in the denominator. This is justified if we are not interested in values of $C_n(t)$ shortly after $t = 0$.

$$\begin{aligned} 1 + 2\pi i\omega f(\omega) &= \frac{2\pi i}{\hbar} < n|H^{(1)}|n > f(\omega) + \frac{1}{\hbar^2}\sum_{k\neq n} | < n|H^{(1)}|k > |^2 \left(\frac{2\pi f(\omega)}{-i\omega_{nk}+\epsilon} \right) \\ &= 2\pi i f(\omega)\frac{< n|H^{(1)}|n >}{\hbar} + \frac{2\pi i f(\omega)}{\hbar^2}\sum_{k\neq n}\frac{| < n|H^{(1)}|k > |^2}{(\omega_{nk}+i\epsilon)} \end{aligned}$$

Consolidate terms with $f(\omega)$ now

$$1 + 2\pi i f(\omega)[\omega - \frac{< n|H^{(1)}|n >}{\hbar} - \frac{1}{\hbar^2}\sum_{k\neq n}\frac{| < n|H^{(1)}|k > |^2}{(\omega_{nk}+i\epsilon)}] = 0$$

Solve for $f(\omega)$ since we are eventually going to flip back into the time domain to get $C_n(t)$

$$2\pi i f(\omega)[-\omega + \frac{< n|H^{(1)}|n >}{\hbar} + \frac{1}{\hbar^2}\sum_{k\neq n}\frac{|< n|H^{(1)}|k >|^2}{(\omega_{nk}+i\epsilon)}] = 1$$

$$2\pi i f(\omega) = \frac{1}{-\omega + \frac{<n|H^{(1)}|n>}{\hbar} + \frac{1}{\hbar^2}\sum_{k\neq n}\frac{|<n|H^{(1)}|k>|^2}{(\omega_{nk}+i\epsilon)}}$$

which simplifies to

$$f(\omega) = \frac{i}{2\pi\left[\omega - \frac{<n|H^{(1)}|n>}{\hbar} - \frac{1}{\hbar^2}\sum_{k\neq n}\frac{|<n|H^{(1)}|k>|^2}{(\omega_{nk}+i\epsilon)}\right]}$$

At this point we want to flip back to the time domain through an inverse Fourier Transform.

From a table of Fourier Transforms (CRC pg 414, Standard Math Tables and Formulas) we have

$$\boxed{e^{-cx+ilx} \Longleftrightarrow \frac{i}{\sqrt{2\pi}(l+ic+\alpha)}} \tag{33.10}$$

provided that $c > 0$ and $x > 0$. Note that the CRC defined the Fourier transforms in a symmetric fashion. We had our 2π consolidated on one transform. Let's therefore rewrite the transform in our notation.

$$e^{-cx+ilx} \Longleftrightarrow \frac{i}{2\pi(l+ic+\alpha)}$$

Also $x = t$ and $\alpha = \omega$ in our case leaving

$$\boxed{e^{-ct+ilx} \Longleftrightarrow \frac{i}{2\pi(l+ic+\omega)}} \tag{33.11}$$

By comparison to our expression

$$\begin{aligned}
\alpha &= \omega \\
l &= -\frac{< n|H^{(1)}|n >}{\hbar} \\
ic &= -\frac{1}{\hbar^2}\sum_{k\neq n}\frac{|< n|H^{(1)}|k >|^2}{(\omega_{nk}+i\epsilon)}
\end{aligned}$$

Therefore we have in the time domain

$$F(t) = e^{i\left[-\frac{<n|H^{(1)}|n>}{\hbar} - \frac{1}{\hbar^2}\sum_{k\neq n}\frac{|<n|H^{(1)}|k>|^2}{(\omega_{nk}+i\epsilon)}\right]t}$$

$$\boxed{F(t) = e^{-\frac{i}{\hbar}\left[<n|H^{(1)}|n> + \frac{1}{\hbar}\sum_{k\neq n}\frac{<n|H^{(1)}|k>|^2}{(\omega_{nk}+i\epsilon)}\right]t}} \tag{33.12}$$

Now the exponent may be converted into a more manageable form by applying

$$\boxed{lim_{\epsilon\to 0}\frac{1}{\omega+i\epsilon} = \wp(\frac{1}{\omega}) - i\pi\delta(\omega)} \tag{33.13}$$

where $\wp$ is called the Cauchy Principle part.

$$\begin{aligned} \wp\frac{1}{\omega} &= \frac{1}{\omega} \text{ if } \omega \neq 0 \\ \wp\frac{1}{\omega} &= 0 \text{ if } \omega = 0 \end{aligned}$$

So as $\epsilon \to 0$

$$F(t) = C_n(t) = e^{-\frac{i}{\hbar}\left[<n|H^{(1)}|n> + \frac{1}{\hbar}\sum_{k\neq n}\frac{|<n|H^{(1)}|k>|^2}{\omega_{nk}}\right]t}$$

$$\begin{aligned} C_n(t) &= e^{-\frac{i}{\hbar}\left[<n|H^{(1)}|n> + \frac{1}{\hbar}\sum_{k\neq n}\left(\frac{|<n|H^{(1)}|k>|^2}{\omega_{nk}} - i\pi|<n|H^{(1)}|k>|^2\delta(\omega_{nk})\right)\right]t} \\ &= e^{-\frac{i}{\hbar}\left[<n|H^{(1)}|n> + \sum_{k\neq n}\left(\frac{|<n|H^{(1)}|k>|^2}{\epsilon_{nk}} - \frac{i\pi}{\hbar}|<n|H^{(1)}|k>|^2\delta(\omega_{nk})\right)\right]t} \\ &= e^{-\frac{i}{\hbar}\left[<n|H^{(1)}|n> + \sum_{k\neq n}\frac{|<n|H^{(1)}|k>|^2}{(\epsilon_n^{(0)}-\epsilon_k^{(0)})}\right]t - \frac{\pi}{\hbar^2}|<n|H^{(1)}|k>|^2\delta(\omega_{nk})t} \end{aligned}$$

Note that from non-degenerate perturbation theory the first term in the exponent is our 1st order correction $\epsilon^{(1)}$ and the second term in the exponent is our 2nd order correction $\epsilon^{(2)}$. So let's just call the stuff in brackets $\Delta\epsilon$.

$$\begin{aligned} \Delta\epsilon &= <n|H^{(1)}|n> + \sum_{k\neq n}\frac{|<n|H^{(1)}|k>|^2}{\epsilon_n^{(0)} - \epsilon_k^{(0)}} \\ &= \epsilon^{(1)} + \epsilon^{(2)} \end{aligned}$$

We now have

$$C_n(t) = e^{\frac{-i\Delta\epsilon t}{\hbar}} e^{-\frac{\pi}{\hbar^2}|<n|H^{(1)}|k>|^2}\delta(\omega_{nk})t$$

where $\delta(\omega_{nk}) = \hbar\delta(\epsilon_{nk})$

$$C_n(t) = e^{\frac{-i\Delta\epsilon t}{\hbar}} e^{-\frac{\pi}{\hbar}|<n|H^{(1)}|k>|^2\delta(\epsilon_{nk})t} \tag{33.14}$$

Now the exponent of the second exponential looks like Fermi's Golden Rule (Γ is a rate $\Gamma = \frac{\pi}{2\hbar}| < n|H^{(1)}|k > |^2\rho(\epsilon_{nk})$) except its off by $\frac{1}{2}$ from our real Fermi Golden rule expression. Compensate for this factor to get

$$C_n(t)e^{-\frac{i\Delta\epsilon t}{\hbar}} e^{-2\Gamma t}$$

or let $2\Gamma = \frac{\Gamma'}{2}$ to get

$$C_n(t) = e^{-\frac{i\Delta\epsilon t}{\hbar}} e^{-\frac{\Gamma' t}{2}}$$

Finally since $P_n(t) = |C_n(t)|^2$

$$\boxed{P_n(t) = e^{\frac{-\Gamma'}{t}}} \tag{33.15}$$

This is the exponential decay of an unstable state. We just proved our intial assertion that the state will intrinsically decay in an exponential fashion.

Finally! (for real) since we have $C_n(t)$ we can solve for $C_k(t)$ and in turn get $P_k(t)$ which is the transition probability into a final state or group of final states that the intial state is bleeding into.

Recall that

$$\begin{aligned}
C_k(t) &= \frac{1}{i\hbar}\int_{t_0}^{t} dt' C_n(t')e^{i\omega_{kn}t'} < k|H^{(1)}|n > \\
&= \frac{1}{i\hbar}\int_{t_0}^{t} dt'[e^{\frac{-i\Delta\epsilon t'}{\hbar}} e^{\frac{-\Gamma' t'}{2}}]e^{i\omega_{kn}t'} < k|H^{(1)}|n > \\
&= \frac{1}{i\hbar}\int_{t_0}^{t} dt' e^{\frac{-i\Delta\epsilon t'}{\hbar}} e^{\frac{-\Gamma' t'}{2}} e^{\frac{i\epsilon_{kn}t'}{\hbar}} < k|H^{(1)}|n > \\
&= \frac{1}{i\hbar}\int_{t_0}^{t} dt' e^{\frac{[i(\epsilon_{kn}-\Delta\epsilon)-\frac{\Gamma'\hbar}{2}]t'}{\hbar}} < k|H^{(1)}|n >
\end{aligned}$$

recall that $H^{(1)}$ is constant so $< k|H^{(1)}|n >$ can come out of the integral.

$$\begin{aligned}
C_k(t) &= \frac{< k|H^{(1)}|n >}{i\hbar} \int_{t_0}^{t} dt' \, e^{\frac{[i(\epsilon_{kn}-\Delta\epsilon)-\frac{\Gamma'\hbar}{2}]t'}{\hbar}} \\
&= \frac{\hbar < k|H^{(1)}|n >}{i\hbar} \left. \frac{e^{\frac{[i(\epsilon_{kn}-\Delta\epsilon)-\frac{\Gamma'\hbar}{2}]t}{\hbar}}}{i(\epsilon_{kn}-\Delta\epsilon)-\frac{\Gamma'\hbar}{2}} \right|_{t_0=0}^{t} \\
&= \frac{< k|H^{(1)}|n >}{i} \left. \frac{e^{\frac{[i(\epsilon_{kn}-\Delta\epsilon)-\frac{\Gamma'\hbar}{2}]t}{\hbar}}}{i(\epsilon_{kn}-\Delta\epsilon)-\frac{\Gamma'\hbar}{2}} \right|_{t_0=0}^{t} \\
&= < k|H^{(1)}|n > \frac{\left[e^{\frac{[i(\epsilon_{kn}-\Delta\epsilon)-\frac{\Gamma'\hbar}{2}]t}{\hbar}} - 1 \right]}{-[(\epsilon_{kn}-\Delta\epsilon)+\frac{i\Gamma'\hbar}{2}]} \\
&= \frac{< k|H^{(1)}|n >}{[(\epsilon_{kn}-\Delta\epsilon)+\frac{i\Gamma'\hbar}{2}]} [1 - e^{\frac{[i(\epsilon_{kn}-\Delta\epsilon)-\frac{\Gamma'\hbar}{2}]t}{\hbar}}]
\end{aligned}$$

We get

$$\boxed{C_k(t) = \frac{<k|H^{(1)}|n>}{[(\epsilon_{kn}-\Delta\epsilon)+\frac{i\Gamma'\hbar}{2}]} \left[1 - e^{\frac{-\Gamma' t}{2}} e^{\frac{i}{\hbar}(\epsilon_{kn}-\Delta\epsilon)t} \right]} \tag{33.16}$$

This is the desired form of the final state time dependent coefficient.

Now for the transition probability.

$$\begin{aligned}
P_k &= |C_k(t)|^2 \\
&= \frac{| < k|H^{(1)}|n > |^2}{[(\epsilon_{kn}-\Delta\epsilon)^2 + \frac{\Gamma^{2\prime}\hbar^2}{4}]} \left(1 - e^{\frac{-\Gamma' t}{2}} e^{ia} \right) \left(1 - e^{\frac{-\Gamma' t}{2}} e^{-ia} \right)
\end{aligned}$$

where $a = \frac{(\epsilon_{kn}-\Delta\epsilon)t}{\hbar}$. After some algebra this works out to be

$$P_k = \frac{| < k|H^{(1)}|n > |^2}{[(\epsilon_{kn}-\Delta\epsilon)^2 + \frac{\Gamma^{2\prime}\hbar^2}{4}]} \left(1 - e^{-\Gamma' t} - 2e^{\frac{-\Gamma' t}{2}} cos \frac{(\epsilon_{kn}-\Delta\epsilon)t}{\hbar} \right)$$

This is the desired expression for the transition probability of the final state

Now as $t \to \infty$

$$\boxed{P_k = \frac{|<k|H^{(1)}|n>|^2}{[(\epsilon_{kn}-\Delta\epsilon)^2 + \frac{\Gamma^{2\prime}\hbar^2}{4}]}} \tag{33.17}$$

where $\epsilon_{kn} = (\epsilon_k - \epsilon_n)$ and where $\Gamma' = \frac{\pi}{2\hbar}| < n|H^{(1)}|k > |^2 \rho(\epsilon_{kn})$. This is back to our Lorentzian lineshape peaked at $\epsilon_k = \epsilon_n + \Delta\epsilon$ and with a spectral width of $\Gamma\hbar$.

Chapter 34

Irreversible decay, Redux

We will derive the previous results in a slightly different way. It is much faster. Start with the time dependent Schrodinger equation expressed in the interaction representation

$$i\hbar\frac{d|\Psi_I(t)>}{dt} = H^{(1)'}|\Psi_I(t)>$$

where in general $|\Psi_I(t)>$ can be expressed as a linear combination of $t = 0$ wavefunctions.

$$|\Psi_I(t)> = \sum_l C_l(t)|l>_I$$

where note that at $t = 0$, $|l>_I = |l>_s$.

Now as before we will ultimately want $C_n(t)$ to get $P_n(t)$. This will show the decay of the initial state.

Multiply both sides of the Schrodinger equation by $< n|$.

$$i\hbar\frac{d}{dt} < n|\Psi_I(t)> = < n|H^{(1)'}|\Psi_I(t)>$$

Now insert the completeness relation ($\sum_k |k>< k| = 1$) above

$$i\hbar\frac{d}{dt} < n|\Psi_I(t)> = \sum_k < n|H^{(1)'}|k>< k|\Psi_I(t)>$$

Now separate the $k = n$ case on the right hand side.

$$i\hbar\frac{d}{dt} < n|\Psi_I(t)> = < n|H^{(1)}|n>< n|\Psi_I(t)> + \sum_{k\neq n} < n|H^{(1)'}|k>< k|\Psi_I(t)>$$

Now divide through both sides by $< n|\Psi_I(t) >$ to consolidate terms

$$\begin{aligned}\frac{i\hbar\frac{d}{dt} < n|\Psi_I(t) >}{< n|\Psi_I(t) >} &= < n|H^{(1)}|n > + \sum_{k\neq n} < n|H^{(1)'}|k > \frac{< k|\Psi_I(t) >}{< n|\Psi_I(t) >} \\ i\hbar ln < n|\Psi_I(t) > &= < n|H^{(1)}|n > + \sum_{k\neq n} < n|H^{(1)'}|k > \frac{< k|\Psi_I(t) >}{< n|\Psi_I(t) >}\end{aligned}$$

Now at this point the above expression can be simplified by noting 2 things.

- a) Our initial state is basically n. That is, $Cn(t) \simeq 1$ (but not necessarily exactly 1) and the perturbation is small. All other time dependent coefficients are ≈ 0. Therefore $< n|\Psi_I(t) > \simeq 1$
- b) From this we also see that $< k|\Psi_I(t) > = \frac{1}{i\hbar}\int_{t_0}^{t} dt^{'} < k|H^{(1)'}(t)|n >$

Replacing these two points into the above expression we get

$$i\hbar ln < n|\Psi_I(t) > = < n|H^{(1)'}|n > + \sum_{k\neq n} < n|H^{(1)'}|k > \frac{1}{i\hbar}\int_{t_0}^{t} dt^{'} < k|H^{(1)'}|n >$$

Now let's convert $H^{(1)'} \rightarrow H^{(1)}$. Recall that in the interaction representation $H^{(1)'} = e^{\frac{iH^{(0)}t}{\hbar}} H^{(1)} e^{\frac{-iH^{(0)}t}{\hbar}}$. We get

$$\begin{aligned} & i\hbar ln < n|\Psi_I(t) > \\ = \ & < n|e^{\frac{iH^{(0)}t}{\hbar}} H^{(1)} e^{\frac{-iH^{(0)}t}{\hbar}}|n > \\ + \ & \sum_{k\neq n} \frac{< n|e^{\frac{iH^{(0)}t}{\hbar}} H^{(1)} e^{\frac{-iH^{(0)}t}{\hbar}}|k >}{i\hbar} \int_{t_0}^{t} dt^{'} < k|e^{\frac{iH^{(0)}t}{\hbar}} H^{(1)} e^{\frac{-iH^{(0)}t}{\hbar}}|n > \\ = \ & e^{\frac{i\epsilon_n^{(0)}t}{\hbar}} < n|H^{(1)}|n > e^{\frac{-i\epsilon_n^{(0)}t}{\hbar}} \\ + \ & \sum_{k\neq n} \frac{e^{\frac{i\epsilon_n^{(0)}t}{\hbar}} < n|H^{(1)}|k > e^{\frac{-i\epsilon_k^{(0)}t}{\hbar}}}{i\hbar} \int_{t_0}^{t} dt^{'} e^{\frac{i\epsilon_n^{(0)}t}{\hbar}} < n|H^{(1)}|k > e^{\frac{-i\epsilon_n^{(0)}t}{\hbar}} \\ = \ & < n|H^{(1)}|n > + \sum_{k\neq n} \frac{e^{\frac{i(\epsilon_n^{(0)}-\epsilon_k^{(0)})t}{\hbar}} < n|H^{(1)}|k >}{i\hbar} \int_{t_0}^{t} dt^{'} e^{\frac{i(\epsilon_k^{(0)}-\epsilon_n^{(0)})t^{'}}{\hbar}} < k|H^{(1)}|n >\end{aligned}$$

where $\omega_{nk} = \frac{\epsilon_n^{(0)}-\epsilon_k^{(0)}}{\hbar}$

$$i\hbar ln < n|\Psi_I(t) > = < n|H^{(1)}|n > + \sum_{k\neq n} \frac{e^{i\omega_{nk}t} < n|H^{(1)}|k >}{i\hbar} \int_{t_0}^{t} dt^{'} e^{i\omega_{nk}t^{'}} < k|H^{(1)}|n >$$

Now here just like we did previously we will assume a time independent (constant) $H^{(1)}$. However, we will add $e^{\eta t}$ in front to allow for a slow turn on. At the end of the problem we can let $\eta \to 0$

$$H^{(1)} = e^{\eta t} H^{(1)}$$

Also call $< n|\Psi_I(t) >= C_n(t)$ so this notation looks familiar like our previous expression in the last chapter.

$$\begin{aligned}
i\hbar lnC_n(t) &= < n|e^{\eta t}H^{(1)}|n > + \sum_{k\neq n} e^{i\omega_{nk}t}\frac{< n|e^{\eta t}H^{(1)}|k >}{i\hbar}\int_{t_0}^{t} dt^{'} e^{-i\omega_{nk}t^{'}} < k|e^{\eta t^{'}}H^{(1)}|n > \\
&= e^{\eta t} < n|H^{(1)}|n > + \sum_{k\neq n} \frac{e^{(i\omega_{nk}+\eta)t} < n|H^{(1)}|k >}{i\hbar}\int_{t_0}^{t} dt^{'} e^{(-i\omega_{nk}+\eta)t^{'}} < k|H^{(1)}|n > \\
&= e^{\eta t} < n|H^{(1)}|n > + \sum_{k\neq n} \frac{e^{(i\omega_{nk}+\eta)t}| < n|H^{(1)}|k > |^2}{i\hbar}\int_{t_0}^{t} dt^{'} e^{(-i\omega_{nk}+\eta)t^{'}} dt^{'}
\end{aligned}$$

Let $t_0 \to \infty$ since the integral contributes little to nothing in this region.

$$i\hbar lnC_n = e^{\eta t} < n|H^{(1)}|n > + \sum_{k\neq n} e^{(i\omega_{nk}+\eta)t}\frac{| < n|H^{(1)}|k > |^2}{i\hbar}\int_{-\infty}^{t} dt^{'} e^{(-i\omega_{nk}+\eta)t^{'}} dt^{'}$$

Now integrate the expression

$$\begin{aligned}
i\hbar lnC_n &= e^{\eta t} < n|H^{(1)}|n > + \sum_{k\neq n} e^{(i\omega_{nk}+\eta)t}\frac{| < n|H^{(1)}|k > |^2}{i\hbar}\left.\frac{e^{(-i\omega_{nk}+\eta)t^{'}}}{(-i\omega_{nk}+\eta)}\right|_{-\infty}^{t} \\
&= e^{\eta t} < n|H^{(1)}|n > + \sum_{k\neq n} e^{(i\omega_{nk}+\eta)t}\frac{| < n|H^{(1)}|k > |^2}{i\hbar}\left[\frac{e^{(-i\omega_{nk}+\eta)t}}{(-i\omega_{nk}+\eta)}\right] \\
&= e^{\eta t} < n|H^{(1)}|n > + \sum_{k\neq n} \frac{e^{2\eta t}| < n|H^{(1)}|k > |^2}{i\hbar(-i\omega_{nk}+\eta)}
\end{aligned}$$

$$lnC_n = \frac{e}{i\hbar}\left[e^{\eta t} < n|H^{(1)}|n > + \sum_{k\neq n} \frac{e^{2\eta t}| < n|H^{(1)}|k > |^2}{i\hbar(-i\omega_{nk}+\eta)}\right]$$

As $\eta \to 0$ ($e^{\eta t}$ and $e^{2\eta t}$ both die quickly).

$$\begin{aligned} lnC_n &\simeq \frac{1}{i\hbar}\left[< n|H^{(1)}|n > + \sum_{k\neq n} \frac{|< n|H^{(1)}|k >|^2}{(-i\epsilon_{nk} + \eta\hbar)}(\frac{1}{i}) \right] \\ &\simeq \frac{1}{i\hbar}\left[< n|H^{(1)}|n > + \sum_{k\neq n} \frac{|< n|H^{(1)}|k >|^2}{(\epsilon_{nk} + i\eta\hbar)} \right] \end{aligned}$$

Integrate this familiar looking expression to get

$$\boxed{C_n(t) \simeq e^{-\frac{i}{\hbar}\left[<n|H^{(1)}|n> + \sum_{k\neq n} \frac{|<n|H^{(1)}|k>|^2}{(\epsilon_{nk} + i\eta\hbar)}\right]}} \tag{34.1}$$

Now the exponent may be connected into a more manegeable form by applying

$$lim_{\eta\to 0}\frac{1}{\omega + i\eta} = \wp\frac{1}{\omega} - i\pi\delta(\omega)$$

where $\wp$ is called the Cauchy Principal part

$$\begin{aligned} \wp\frac{1}{\omega} &= \frac{1}{\omega} \text{ if } \omega \neq 0 \\ \wp\frac{1}{\omega} &= 0 \text{ if } \omega = 0 \end{aligned}$$

So as $\eta \to 0$

$$\begin{aligned} C_n(t) &= e^{-\frac{i}{\hbar}\left[<n|H^{(1)}|n> + \sum_{k\neq n}\left(\frac{|<n|H^{(1)}|k>|^2}{\epsilon_{nk}} - i\pi|<n|H^{(1)}|k>|^2\delta(\epsilon_{nk})\right)\right]t} \\ &= e^{-\frac{i}{\hbar}\left[<n|H^{(1)}|n> + \sum_{k\neq n}\frac{|<n|H^{(1)}|k>|^2}{(\epsilon_n^{(0)} - \epsilon_k^{(0)})}\right]t - \frac{\pi}{\hbar}\sum_{k\neq n}|<n|H^{(1)}|k>|^2\delta(\epsilon_{nk})t} \end{aligned}$$

Again, recall that from non-degenerate perturbation theory, the term in brackets is our 1st and 2nd order energy corrections ($\epsilon^{(1)}$ and $\epsilon^{(2)}$). So let's just call the stuff in brackets $\Delta\epsilon$

$$\begin{aligned} \Delta\epsilon &= < n|H^{(1)}|n > + \sum_{k\neq n} \frac{|< n|H^{(1)}|k >|^2}{\epsilon_n^{(0)} - \epsilon_k^{(0)}} \\ &= \epsilon^{(1)} + \epsilon^{(2)} \end{aligned}$$

$$C_n(t) = e^{\frac{-i\Delta\epsilon t}{\hbar}} e^{-\frac{\pi}{\hbar}\sum_{k\neq n}|<n|H^{(1)}|k>|^2\delta(\epsilon_{nk})t}$$

Now note that the second exponent looks like our Fermi's Golden Rule rate $\Gamma = \frac{\pi}{2\hbar}| < n|H^{(1)}|k > |^2\rho(\epsilon_{nk})$ except that it is off by $\frac{1}{2}$.

$$C_n(t) = e^{\frac{-i\Delta\epsilon t}{\hbar}} e^{-2\Gamma t}$$

Let $2\Gamma = \frac{\Gamma^{'}}{2}$

$$C_n(t) = e^{\frac{-i\Delta\epsilon t}{\hbar}} e^{\frac{-\Gamma^{'} t}{2}}$$

Now we can find the probability $P_n(t)$

$$P_n(t) = |C_n(t)|^2 = e^{-\Gamma^{'} t}$$

$$\boxed{P_n(t) = e^{-\Gamma^{'} t}} \tag{34.2}$$

This represents the exponential decay of the initial state as we derived previously. In fact the expressions are identical.

Now one can go and find $P_k(t)$ but since this is identical to the previous derivation we just simply reproducte the result here.

$$\boxed{P_{k,t\rightarrow\infty}(t) = \frac{|<k|H^{(1)}|n>|^2}{\left[(\epsilon_{kn} - \Delta\epsilon)^2 + \frac{\Gamma^{2'}\hbar^2}{4}\right]}} \tag{34.3}$$

where $\epsilon_{kn} = \epsilon_k - \epsilon_n$ and where $\Gamma^{'} = 4\Gamma$ and $\Gamma = \frac{\pi}{2\hbar}| < n|H^{(1)}|k > |^2\rho(\epsilon_{nk})$. This is our Lorentzian lineshape for the other state. This can be considered as absorption broadening of a transition due to an unstable initial state.

Chapter 35

Maxwell's equations (and units)

When working with Maxwell's equations watch out for the units being used. Maxwell's equations will look different with different units. Authors sometimes don't mention overtly what basis they are using making it easy for you to get into trouble. (Some people like CGS because the equations are more symmetric). Below are the diferential forms of Maxwell's equations in the absence of magnetic or polarizable media.

SI	CGS
$\vec{\nabla} \cdot \vec{E} = \dfrac{\rho}{\epsilon_0}$	$\vec{\nabla} \cdot \vec{E} = 4\pi \dfrac{\rho}{\epsilon_0}$
$\vec{\nabla} \times \vec{E} = -\dfrac{\partial \vec{B}}{\partial t}$	$\vec{\nabla} \times \vec{E} = -\dfrac{1}{c}\dfrac{\partial \vec{B}}{\partial t}$
$\vec{\nabla} \cdot \vec{B} = 0$	$\vec{\nabla} \cdot \vec{B} = 0$
$\vec{\nabla} \times \vec{B} = \mu_0 \vec{J} + \dfrac{1}{c^2}\dfrac{\partial \vec{E}}{\partial t}$	$\vec{\nabla} \times \vec{B} = \dfrac{4\pi}{c}\vec{J} + \dfrac{1}{c}\dfrac{\partial \vec{E}}{\partial t}$

Energy density:

SI	CGS
$u = \dfrac{1}{2}\left(\epsilon_0 \lvert\vec{E}\rvert^2 + \dfrac{1}{\mu_0}\lvert\vec{B}\rvert^2\right)$	$u = \dfrac{1}{8\pi}\left(\lvert\vec{E}\rvert^2 + \lvert\vec{B}\rvert^2\right)$

where in all cases

$$
\begin{aligned}
\vec{E} &= \text{electric field} \\
\vec{B} &= \text{magnetic field} \\
\vec{J} &= \text{current density} \\
\rho &= \text{charge density} \\
\epsilon_0 &= \text{electrical permittivity in vacuum} \\
\mu_0 &= \text{magnetic permeability in vacuum}
\end{aligned}
$$

Chapter 36

Maxwell's equations (Electric and Magnetic Fields)

Here we will briefly review E and M since what follows this will be a more detailed description about the interaction of light and matter.

Previously we considered things semiclassically. We treated light as waves and matter quantum mechanically. But this semiclassical treatment is not strictly correct because in reality *both* light and matter should be treated quantum mechanically.

One glaring inadequacy of our previous semiclassical treatment of light-matter interaction is the failure to predict spontaneous emission. We got absorption and stimulated emission but we never found one for this third important process.

In SI units let's start out with Maxwell's equations and assume no stray charges are present ($\rho = 0$) and that no currents are present ($\vec{J} = 0$).

$$\vec{\nabla} \cdot \vec{E} = 0 \qquad \text{(assumes no charges)} \tag{36.1}$$

$$\vec{\nabla} \cdot \vec{B} = 0 \qquad \text{(assumes no magnetic monopoles)} \tag{36.2}$$

$$\vec{\nabla} \times \vec{E} = -\frac{\partial \vec{B}}{\partial t} \tag{36.3}$$

$$\vec{\nabla} \times \vec{B} = \frac{1}{c^2}\frac{\partial \vec{E}}{\partial t} = \mu_0 \epsilon_0 \frac{\partial \vec{E}}{\partial t} \qquad \text{(assumes no currents)} \tag{36.4}$$

Now rather than work directly with $\vec{E}$ and $\vec{B}$ it turns out to be more convenient to work with two related quantities called the vector potential

$\vec{A}$ associated with the magnetic field and the scalar potential ϕ associated with the electric field.

One simplification from this is that it allows us to describe $\vec{E}$ and $\vec{B}$ not with 6 quantities (3 for both $\vec{E}$ and $\vec{B}$) but rather 4 (one for the scalar potential and 3 for the vector potential).

Using $\vec{A}$ is also particularly convenient because as we will see it arises naturally in the Hamiltonian for a charged particle in the presence of a field.

In the work that follows we will need three vector math relations:

$$\begin{array}{lll} \text{(A)} & \vec{\nabla} \cdot \left(\vec{\nabla} \times \vec{F}\right) = 0 & \text{(divergence of a curl is 0)} \\ \text{(B)} & \vec{\nabla} \times \left(\vec{\nabla} F\right) = 0 & \text{(curl of a gradient is 0)} \\ \text{(C)} & \vec{\nabla} \times \left(\vec{\nabla} \times \vec{F}\right) = \vec{\nabla}(\vec{\nabla} \cdot \vec{F}) - \vec{\nabla}^2 \vec{F} & \end{array}$$

A word on notation: $\nabla \equiv$ *del* $\equiv$ *grad*.

Now proof of (A):

$$\begin{pmatrix} \frac{\partial}{\partial x} & \frac{\partial}{\partial y} & \frac{\partial}{\partial z} \end{pmatrix} \cdot \begin{pmatrix} i & j & k \\ \frac{\partial}{\partial x} & \frac{\partial}{\partial y} & \frac{\partial}{\partial z} \\ A_x & A_y & A_z \end{pmatrix} =$$

$$\begin{aligned} &= \left(\tfrac{\partial}{\partial x} \quad \tfrac{\partial}{\partial y} \quad \tfrac{\partial}{\partial z}\right) \cdot \left[i \left(\tfrac{\partial A_z}{\partial y} - \tfrac{\partial A_y}{\partial z} \right) \quad -j \left(\tfrac{\partial A_z}{\partial x} - \tfrac{\partial A_x}{\partial z} \right) \quad k \left(\tfrac{\partial A_y}{\partial x} - \tfrac{\partial A_x}{\partial y} \right) \right] \\ &= \frac{\partial}{\partial x} \left[\frac{\partial A_z}{\partial y} - \frac{\partial A_y}{\partial z} \right] - \frac{\partial}{\partial y} \left[\frac{\partial A_z}{\partial x} - \frac{\partial A_x}{\partial z} \right] + \frac{\partial}{\partial z} \left[\frac{\partial A_y}{\partial x} - \frac{\partial A_x}{\partial y} \right] \\ &= \frac{\partial^2 A_z}{\partial x \partial y} - \frac{\partial^2 A_y}{\partial x \partial z} - \frac{\partial^2 A_z}{\partial y \partial x} + \frac{\partial^2 A_x}{\partial y \partial z} + \frac{\partial^2 A_y}{\partial z \partial x} - \frac{\partial^2 A_x}{\partial z \partial y} = 0 \end{aligned}$$

(Note we are not dealing with QM right now, more loose on the order of operation.)

Proof of (B):

$$\vec{\nabla} \times \left(\vec{\nabla} F\right) = 0$$

where

$$\vec{\nabla} F = \left(\frac{\partial F}{\partial x}, \frac{\partial F}{\partial y}, \frac{\partial F}{\partial z} \right)$$

and $\vec{\nabla} \times \left(\vec{\nabla} F\right)$ is

$$\begin{vmatrix} \vec{i} & \vec{j} & \vec{k} \\ \frac{\partial}{\partial x} & \frac{\partial}{\partial y} & \frac{\partial}{\partial z} \\ \frac{\partial F}{\partial x} & \frac{\partial F}{\partial y} & \frac{\partial F}{\partial x} \end{vmatrix} = \vec{i}\left(\frac{\partial^2 F}{\partial y \partial z} - \frac{\partial^2 F}{\partial y \partial z}\right) - \vec{j}\left(\frac{\partial^2 F}{\partial x \partial z} - \frac{\partial^2 F}{\partial x \partial z}\right) + \vec{k}\left(\frac{\partial^2 F}{\partial x \partial y} - \frac{\partial^2 F}{\partial x \partial y}\right) = 0$$

Now start with Maxwell's Equation (2) $\vec{\nabla} \cdot \vec{B} = 0$. By math relation (A) $\vec{B}$ must be the curl of something. Call this something $\vec{A}$, the vector potential.

$$\boxed{\vec{B} = \vec{\nabla} \times \vec{A}} \tag{36.5}$$

Now using this relation for $\vec{B}$ plug it into Maxwell equation (3)

$$\begin{aligned} \vec{\nabla} \times \vec{E} &= -\frac{\partial \vec{B}}{\partial t} \\ \vec{\nabla} \times \vec{E} &= -\frac{\partial}{\partial t}\left(\vec{\nabla} \times \vec{A}\right) \\ \vec{\nabla} \times \vec{E} &= -\vec{\nabla} \times \frac{\partial \vec{A}}{\partial t} \\ \vec{\nabla} \times \vec{E} + \vec{\nabla} \times \frac{\partial \vec{A}}{\partial t} &= 0 \\ \vec{\nabla} \times \left(\vec{E} + \frac{\partial \vec{A}}{\partial t}\right) &= 0 \end{aligned}$$

Now since vector math relation (B) says that $\vec{\nabla} \times \left(\vec{\nabla}\phi\right) = 0$, by inspection we associate $\vec{\nabla}\phi$ with $\left(\vec{E} + \frac{\partial \vec{A}}{\partial t}\right)$. Also an extra sign is added to $\vec{\nabla}\phi$ for convenience.

$$-\vec{\nabla}\phi = \left(\vec{E} + \frac{\partial \vec{A}}{\partial t}\right)$$

or

$$\boxed{\vec{E} = -\vec{\nabla}\phi - \tfrac{\partial \vec{A}}{\partial t}} \tag{36.6}$$

Summary

We have now re-expressed $\vec{E}$ and $\vec{B}$ in terms of ϕ and $\vec{A}$.

$$\vec{B} = \vec{\nabla} \times \vec{A} \tag{36.7}$$

$$\vec{E} = -\vec{\nabla}\phi - \frac{\partial \vec{A}}{\partial t} \tag{36.8}$$

However right now there are an infinite number of possible choices (combinations of ϕ and $\vec{A}$) that will work. (There are many "gauges"). So we have to impose some constraints (*i.e.* choose a particular gauge eventually).

To demonstrate the many possibilities let $\vec{A}' = \vec{A} + \vec{\nabla}\chi$ where χ is any function of $\vec{r}$ and t.

$$\vec{B} = \vec{\nabla} \times \vec{A}'$$
$$\vec{B} = \vec{\nabla} \times \left(\vec{A} + \vec{\nabla}\chi\right)$$
$$\vec{B} = \vec{\nabla} \times \vec{A} + \left(\vec{\nabla} \times \vec{\nabla}\chi\right)$$

But we know from vector math relation (B) that $\vec{\nabla} \times \vec{\nabla}\chi = 0$ so $\vec{B} = \vec{\nabla} \times \vec{A}$ or $\vec{B} = \vec{\nabla} \times \vec{A}'$ are the same thing.

Similarly we can show the same for ϕ.

Let $\vec{A}' = \vec{A} + \vec{\nabla}\chi$, put this into

$$\vec{E} = -\vec{\nabla}\phi - \frac{\partial \vec{A}}{\partial t}$$
$$\vec{E} = -\vec{\nabla}\phi - \frac{\partial}{\partial t}\left(\vec{A}' - \vec{\nabla}\chi\right)$$
$$\vec{E} = -\vec{\nabla}\phi - \frac{\partial \vec{A}'}{\partial t} + \frac{\partial(\vec{\nabla}\chi)}{\partial t}$$

$$\vec{E} = -\vec{\nabla}\phi - \frac{\partial \vec{A}'}{\partial t} + \frac{\vec{\nabla}\partial\chi}{\partial t}$$
$$\vec{E} = -\vec{\nabla}\phi + \frac{\vec{\nabla}\partial\chi}{\partial t} - \frac{\partial \vec{A}'}{\partial t}$$
$$\vec{E} = -\vec{\nabla}\left(\phi - \frac{\partial\chi}{\partial t}\right) - \frac{\partial \vec{A}'}{\partial t}$$

Call $\phi' = (\phi - \frac{\partial\chi}{\partial t})$

$$\vec{E} = -\vec{\nabla}\phi' - \frac{\partial \vec{A}'}{\partial t}$$

where χ is again any function of $\vec{r}$ and t.

Summary

General forms of $\vec{A}$ and ϕ

$$\boxed{\vec{A}' = \vec{A} + \vec{\nabla}\chi} \tag{36.9}$$

$$\boxed{\phi' = \phi - \tfrac{\partial \chi}{\partial t}} \tag{36.10}$$

where χ is any function of (r, t)

Now let's go back to Maxwell's equation (4)

$$\vec{\nabla} \times \vec{B} = \mu_0 \epsilon_0 \frac{\partial \vec{E}}{\partial t}$$

where now $\vec{B} = \vec{\nabla} \times \vec{A}$ and $\vec{E} = -\vec{\nabla}\phi - \frac{\partial \vec{A}}{\partial t}$.

$$\vec{\nabla} \times (\vec{\nabla} \times \vec{A}) = \mu_0 \epsilon_0 \frac{\partial}{\partial t}\left(-\vec{\nabla}\phi - \frac{\partial \vec{A}}{\partial t}\right)$$

Now we have to involve vector math relation (3)

$$\vec{\nabla} \times \left(\vec{\nabla} \times \vec{F}\right) = \vec{\nabla}(\vec{\nabla} \cdot \vec{F}) - \vec{\nabla}^2 \vec{F}$$

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

$$\vec{\nabla}(\vec{\nabla} \cdot \vec{A}) - \vec{\nabla}^2 \vec{A} = -\mu_0 \epsilon_0 \frac{\vec{\nabla}\partial\phi}{\partial t} - \mu_0 \epsilon_0 \frac{\partial^2 \vec{A}}{\partial t^2}$$

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

$$-\nabla^2 A + \mu_o \epsilon_o \frac{\partial^2 A}{\partial t^2} + \nabla\left[\nabla \cdot A + \mu_o \epsilon_o \frac{\partial \phi}{\partial t}\right] = 0$$

Life would be great if the last two terms were 0 since then we have the wave equation for $\vec{A}$.

So the Lorentz gauge is invoked where its constraint is

$$\boxed{\vec{\nabla} \cdot \vec{A} + \mu_0 \epsilon_0 \frac{\partial \phi}{\partial t} = 0} \tag{36.11}$$

leaving

$$-\vec{\nabla}^2 \vec{A} + \mu_0 \epsilon_0 \frac{\partial^2 \vec{A}}{\partial t^2} = 0$$

or

$$\boxed{\vec{\nabla}^2 \vec{A} - \mu_0 \epsilon_0 \frac{\partial^2 \vec{A}}{\partial t^2} = 0} \tag{36.12}$$

or

$$\boxed{\vec{\nabla}^2 \vec{A} - \frac{1}{c^2} \frac{\partial^2 \vec{A}}{\partial t^2} = 0} \tag{36.13}$$

Keep going, we will derive a similar expression for ϕ.
Using Maxwell equation (1)

$$\vec{\nabla} \cdot \vec{E} = 0$$

use

$$\vec{E} = -\vec{\nabla}\phi - \frac{\partial \vec{A}}{\partial t}$$

$$\vec{\nabla} \cdot \left(-\vec{\nabla}\phi - \frac{\partial \vec{A}}{\partial t} \right) = 0$$

$$-\vec{\nabla} \cdot \vec{\nabla}\phi - \frac{\partial}{\partial t} \left(\vec{\nabla} \cdot \vec{A} \right) = 0$$

where

$$\vec{\nabla} \cdot \vec{A} = -\mu_0 \epsilon_0 \frac{\partial \phi}{\partial t} \tag{36.14}$$

from the Lorentz condition.

$$-\vec{\nabla} \cdot \vec{\nabla}\phi + \mu_0 \epsilon_0 \frac{\partial}{\partial t} \left(\frac{\partial \phi}{\partial t} \right) = 0$$

$$-\vec{\nabla} \cdot \vec{\nabla}\phi + \mu_0 \epsilon_0 \frac{\partial^2 \phi}{\partial t^2} = 0$$

$$-\vec{\nabla}^2 \phi + \mu_0 \epsilon_0 \frac{\partial^2 \phi}{\partial t^2} = 0$$

$$\boxed{\vec{\nabla}^2 \phi - \frac{1}{c^2} \frac{\partial^2 \phi}{\partial t^2} = 0} \tag{36.15}$$

Summary

$$\boxed{\vec{\nabla}^2\vec{A} - \tfrac{1}{c^2}\tfrac{\partial^2\vec{A}}{\partial t^2} = 0} \tag{36.16}$$

$$\boxed{\vec{\nabla}^2\phi - \tfrac{1}{c^2}\tfrac{\partial^2\phi}{\partial t^2} = 0} \tag{36.17}$$

But recall that ϕ and $\vec{A}$ are in general *not* unique.

$$\vec{A'} = \vec{A} + \vec{\nabla}\chi$$

$$\phi' = \phi - \frac{\partial\chi}{\partial t}$$

The Lorentz condition then gives us a way of choosing a gauge

$$\vec{\nabla}\cdot\vec{A} = -\mu_0\epsilon_0\frac{\partial\phi}{\partial t}$$

$$\vec{\nabla}\cdot(\vec{A}+\vec{\nabla}\chi) = -\mu_0\epsilon_0\frac{\partial}{\partial t}\left(\phi - \frac{\partial\chi}{\partial t}\right)$$

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

$$\vec{\nabla}\cdot\vec{A} + \vec{\nabla}^2\chi + \mu_0\epsilon_0\frac{\partial\phi}{\partial t} - \mu_0\epsilon_0\frac{\partial^2\chi}{\partial t^2} = 0$$

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

$$\vec{\nabla}^2\chi - \mu_0\epsilon_0\frac{\partial^2\chi}{\partial t^2} = -\vec{\nabla}\cdot\vec{A} - \mu_0\epsilon_0\frac{\partial\phi}{\partial t}$$

But from the Lorentz condition

$$\vec{\nabla}\cdot\vec{A} = -\mu_0\epsilon_0\frac{\partial\phi}{\partial t}$$

$$\boxed{\vec{\nabla}^2\chi - \mu_0\epsilon_0\tfrac{\partial^2\chi}{\partial t^2} = 0} \tag{36.18}$$

This equation provides a criteria for choosing a gauge when transforming between gauges.

Here we assume a free electromagnetic field with no current, no stray charges and of course no magnetic monopoles.

Now we go and solve for $\vec{A}$.

$$\vec{\nabla}^2\vec{A} - \frac{1}{c^2}\frac{\partial^2\vec{A}}{\partial t^2} = 0 \tag{36.19}$$

The general solutions to the wave equation are of the form

$$\vec{A} = \vec{A_0}\cos\left(\omega t - \vec{k}\cdot\vec{r} + \phi_p\right) \tag{36.20}$$

where

$$\begin{aligned}
&\omega^2 = (kc)^2\\
&\omega = 2\pi\nu\\
&k = \frac{2\pi}{\lambda} = \frac{\omega}{c}\\
&\phi_p = \text{phase shift}\\
&\vec{A_0} = \text{amplitude and direction}\\
&\omega = \text{frequency}\\
&k = \text{wavevector.}
\end{aligned}$$

From this expression of the vector potential we can derive an expression for the electric field $\vec{E}$

$$\vec{E} = -\vec{\nabla}\phi - \frac{\partial\vec{A}}{\partial t}$$

Now we will assume that the scalar potential is constant so that

$$\vec{E} = -\frac{\partial\vec{A}}{\partial t} \tag{36.21}$$

$$\begin{aligned}
\vec{E} &= \vec{A_0}\sin\left(\omega t - \vec{k}\cdot\vec{r} + \phi_p\right)(\omega)\\
\vec{E} &= \omega\vec{A_0}\sin\left(\omega t - \vec{k}\cdot\vec{r} + \phi_p\right) \qquad (36.22)
\end{aligned}$$

Desired expression for the electric field.

Furthermore, from the Lorentz gauge constrain $\nabla\cdot A + \mu_o\epsilon_o\frac{\partial\phi}{\partial t}$, and the assumption of a constant scalar potential (ϕ const) we get $\vec{\nabla}\cdot\vec{A} = 0$ and using $\vec{A} = \vec{A_0}\cos\left(\omega t - \vec{k}\cdot\vec{r} + \phi_p\right)$

$$\vec{A} = \Big(A_{0x}\cos\left(\omega t - \vec{k}\cdot\vec{r} + \phi_p\right), A_{0y}\cos\left(\omega t - \vec{k}\cdot\vec{r} + \phi_p\right), A_{0z}\cos\left(\omega t - \vec{k}\cdot\vec{r} + \phi_p\right)\Big)$$

$$
\begin{aligned}
\vec{\nabla}\cdot\vec{A} &= \frac{\partial A}{\partial x}+\frac{\partial A}{\partial y}+\frac{\partial A}{\partial z}=0 \\
&= -k_x A_{0x}\sin(\omega t-\vec{k}\cdot\vec{r}+\phi_p)-k_y A_{0y}\sin(\omega t-\vec{k}\cdot\vec{r}+\phi_p)-k_z A_{0z}\sin(\omega t-\vec{k}\cdot\vec{r}+\phi_p) \\
&= -\vec{k}\cdot\vec{A_0}\sin(\omega t-\vec{k}\cdot\vec{r}+\phi_p)=0
\end{aligned}
$$

For this to be true $\vec{k}\cdot\vec{A_0}=0$ so $\vec{k}$ is $\perp$ to $\vec{A_0}$ and $\vec{E}\parallel\vec{A_0}$.

Now just as we found an expression for $\vec{E}$, let's go find an expression for $\vec{B}$.

Since $\vec{B}=\vec{\nabla}\times\vec{A}$ and

$$
\vec{A}=\Big(A_{0x}\cos(\omega t-\vec{k}\cdot\vec{r}+\phi_p),A_{0y}\cos(\omega t-\vec{k}\cdot\vec{r}+\phi_p),A_{0z}\cos(\omega t-\vec{k}\cdot\vec{r}+\phi_p)\Big)
$$

$$
\vec{A}=\Big(A_{0x}\cos(a-\vec{k}\cdot\vec{r}),A_{0y}\cos(a-\vec{k}\cdot\vec{r}),A_{0z}\cos(a-\vec{k}\cdot\vec{r})\Big)
$$

where $a=(\omega t+\phi_p)$

$$
\vec{B}=\vec{\nabla}\times\vec{A}=\begin{bmatrix}\vec{i} & \vec{j} & \vec{k}\\ \frac{\partial}{\partial x} & \frac{\partial}{\partial y} & \frac{\partial}{\partial z}\\ A_x\cos(a-\vec{k}\cdot\vec{r}) & A_y\cos(a-\vec{k}\cdot\vec{r}) & A_z\cos(a-\vec{k}\cdot\vec{r})\end{bmatrix}
$$

$$
\begin{aligned}
\vec{B}=&\vec{i}\left[A_z\frac{\cos(a-\vec{k}\cdot\vec{r})}{\partial y}-A_y\frac{\cos(a-\vec{k}\cdot\vec{r})}{\partial z}\right]-\vec{j}\left[A_z\frac{\cos(a-\vec{k}\cdot\vec{r})}{\partial x}-A_x\frac{\cos(a-\vec{k}\cdot\vec{r})}{\partial z}\right] \\
&+\vec{k}\left[A_y\frac{\partial\cos(a-\vec{k}\cdot\vec{r})}{\partial x}-A_x\frac{\cos(a-\vec{k}\cdot\vec{r})}{\partial y}\right] \\
=&\vec{i}\left[A_z(+k_y)\sin(a-\vec{k}\cdot\vec{r})-A_yk_z\sin(a-\vec{k}\cdot\vec{r})\right]-\vec{j}\left[A_zk_x\sin(a-\vec{k}\cdot\vec{r})-A_xk_z\sin(a-\vec{k}\cdot\vec{r})\right] \\
&+\vec{k}\left[A_yk_x\sin(a-\vec{k}\cdot\vec{r})-A_xk_y\sin(a-\vec{k}\cdot\vec{r})\right]
\end{aligned}
$$

For convenience, extract the $\sin(a-\vec{k}\cdot\vec{r})$ common to all terms. This leaves

$$
\Big(\vec{i}\,[A_z(+k_y)-A_yk_z]-\vec{j}\left[A_zk_x-A_xk_z+\vec{k}\right]+\vec{k}\,[A_yk_x-A_xk_y]\Big)\sin(a-\vec{k}\cdot\vec{r})
$$

Claim that the above expression is equivalent to $(\vec{k}\times\vec{A})[-\sin(-\vec{k}\cdot\vec{r}+a)]$

$$(\vec{k} \times \vec{A}) = \begin{vmatrix} \vec{i} & \vec{j} & \vec{k} \\ k_x & k_y & k_z \\ A_x & A_y & A_z \end{vmatrix}$$

$$= \vec{i}[k_y A_z - k_z A_y] - \vec{j}[k_x A_z - k_z A_x] + \vec{k}[k_x A_y - k_y A_x]$$

(So yes, the terms are equivalent)

Therefore,

$$\vec{B} = \vec{\nabla} \times \vec{A} = (\vec{k} \times \vec{A_0}) \sin(a - \vec{k} \cdot \vec{r})$$

where $a = \omega t + \phi_p$.

$$\vec{B} = (\vec{k} \times \vec{A_0}) \sin(\omega t - \vec{k} \cdot \vec{r} + \phi_p) \tag{36.23}$$

Desired expression for $\vec{B}$. So you can immediately see from $(\vec{k} \times \vec{A_0})$ that $\vec{B}$ is $\perp$ to $\vec{k}$ and to A_0.

Visual summary

$$\vec{E} \parallel \vec{A_0}$$
$$\vec{k} \perp \vec{A_0}$$
$$\vec{k} \perp \vec{B}$$
$$\vec{E} \perp \vec{B}$$

$\vec{E}$ and $\vec{B}$ have the same frequency and the same phase.

Chapter 37

Maxwell's equations ver. 2.0 (More general)

$$\vec{\nabla}\cdot\vec{E} = \frac{\rho}{\epsilon_0}\text{(where } \rho = \text{charge density, if no charges are present then} = 0 \text{ like before)} \tag{37.1}$$

(where ρ =charge density, if no charges are present then = 0 like before)

$$\vec{\nabla}\cdot\vec{B} = 0 \tag{37.2}$$

(still assumes no magnetic monopoles)

$$\vec{\nabla}\times\vec{E} = -\frac{\partial\vec{B}}{\partial t} \tag{37.3}$$

$$\vec{\nabla}\times\vec{B} = \mu_0\vec{J} + \mu_0\epsilon_0\frac{\partial\vec{E}}{\partial t} \tag{37.4}$$

(where $\vec{J}$ =current density, if no currents then = 0 like before)

Run through the same argument. Desire $\vec{A}$ and ϕ where $\vec{A}$ is a vector potential and ϕ is a scalar potential.

Use math relations

$$\begin{array}{ll} \text{(A)} & \vec{\nabla}\cdot\left(\vec{\nabla}\times\vec{F}\right) = 0 \\ \text{(B)} & \vec{\nabla}\times\left(\vec{\nabla}F\right) = 0 \end{array}$$

Look at Maxwell (2) $\vec{\nabla}\cdot\vec{B} = 0$. To be true

$$\vec{B} = (\vec{\nabla}\times\vec{A}) \tag{37.5}$$

from math relation (A).

Now use this on Maxwell (3)

$$\vec{\nabla} \times \vec{E} = -\frac{\partial \vec{B}}{\partial t}$$

where $\vec{B} = \vec{\nabla} \times \vec{A}$.

$$\vec{\nabla} \times \vec{E} = -\vec{\nabla} \times \frac{\partial \vec{A}}{\partial t}$$

$$\vec{\nabla} \times \vec{E} + \vec{\nabla} \times \frac{\partial \vec{A}}{\partial t} = 0$$

$$\vec{\nabla} \times \left(\vec{E} + \frac{\partial \vec{A}}{\partial t}\right) = 0$$

therefore

$$\vec{E} + \frac{\partial \vec{A}}{\partial t} = -\vec{\nabla}\phi \qquad \text{choose (-) for convenience}$$

$$\vec{E} = -\vec{\nabla}\phi - \frac{\partial \vec{A}}{\partial t} \tag{37.6}$$

Again there are an infinite number of combinations of ϕ and $\vec{A}$ that work.

Summary

$$\vec{B} = (\vec{\nabla} \times \vec{A}) \tag{37.7}$$

$$\vec{E} = -\vec{\nabla}\phi - \frac{\partial \vec{A}}{\partial t} \tag{37.8}$$

Recall the general forms of $\vec{A}$ and ϕ are

$$\vec{A}' = \vec{A} + \vec{\nabla}\chi \tag{37.9}$$

$$\phi' = \phi - \frac{\partial \chi}{\partial t} \tag{37.10}$$

where $\chi = f(\vec{r}, t)$.

Use Maxwell's (1) and (4) now.

$$\vec{\nabla} \times \vec{B} = \mu_0 \vec{J} + \mu_0 \epsilon_0 \frac{\partial \vec{E}}{\partial t}$$

where

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

$$\vec{E} = -\vec{\nabla}\phi - \frac{\partial \vec{A}}{\partial t}$$

$$\vec{\nabla} \times (\vec{\nabla} \times \vec{A}) = \mu_0\epsilon_0 \frac{\partial}{\partial t}\left[-\vec{\nabla}\phi - \frac{\partial \vec{A}}{\partial t}\right] + \mu_0 \vec{J}$$

Employ another vector relation

$$\vec{\nabla} \times (\vec{\nabla} \times \vec{F}) = \vec{\nabla}(\vec{\nabla} \cdot \vec{F}) - \vec{\nabla}^2 \vec{F} \qquad (37.11)$$

$$\vec{\nabla}(\vec{\nabla} \cdot \vec{A}) - \vec{\nabla}^2 \vec{A} = \mu_0\epsilon_0 \left[-\vec{\nabla}\frac{\partial \phi}{\partial t} - \frac{\partial^2 \vec{A}}{\partial t^2}\right] + \mu_0 \vec{J}$$

$$-\vec{\nabla}^2 \vec{A} + \mu_0\epsilon_0 \frac{\partial^2 \vec{A}}{\partial t^2} + \vec{\nabla}(\vec{\nabla} \cdot \vec{A}) + \mu_0\epsilon_0 \vec{\nabla}\frac{\partial \phi}{\partial t} - \mu_0 \vec{J} = 0$$

$$-\vec{\nabla}^2 \vec{A} + \mu_0\epsilon_0 \frac{\partial^2 \vec{A}}{\partial t^2} + \vec{\nabla}\left[(\vec{\nabla} \cdot \vec{A}) + \mu_0\epsilon_0 \frac{\partial \phi}{\partial t}\right] - \mu_0 \vec{J} = 0$$

we want the terms in the bracket to vanish.

Again assume no currents ($\vec{J} = 0$).

Assume Lorentz gauge and associated constraint

$$\vec{\nabla} \cdot \vec{A} + \mu_0\epsilon_0 \frac{\partial \phi}{\partial t} = 0 \qquad (37.12)$$

Leaving

$$\vec{\nabla}^2 \vec{A} - \mu_0\epsilon_0 \frac{\partial^2 \vec{A}}{\partial t^2} = 0 \qquad \text{(wave equation)} \qquad (37.13)$$

$$\vec{\nabla} \cdot \vec{E} = 0$$

where

$$\vec{E} = -\vec{\nabla}\phi - \frac{\partial \vec{A}}{\partial t}$$

$$\vec{\nabla} \cdot \left(-\vec{\nabla}\phi - \frac{\partial \vec{A}}{\partial t}\right) = 0$$

$$-\vec{\nabla}\cdot\vec{\nabla}\phi - \frac{\vec{\nabla}\cdot\partial\vec{A}}{\partial t} = 0$$

$$-\vec{\nabla}^2\phi - \frac{\partial}{\partial t}\vec{\nabla}\cdot\vec{A} = 0$$

and

$$\vec{\nabla}\cdot\vec{A} = -\mu_0\epsilon_0\frac{\partial\phi}{\partial t}$$

from above Lorentz gauge.

$$-\vec{\nabla}^2\phi + \frac{\partial}{\partial t}\left[\mu_0\epsilon_0\frac{\partial\phi}{\partial t}\right] = 0$$

$$-\vec{\nabla}^2\phi + \mu_0\epsilon_0\frac{\partial^2\phi}{\partial t^2} = 0$$

$$\vec{\nabla}^2\phi - \mu_0\epsilon_0\frac{\partial^2\phi}{\partial t^2} = 0 \qquad \text{wave equation 2} \tag{37.14}$$

Recall that ϕ and $\vec{A}$ in general are not unique. There must be constraints on $\vec{X} = f(\vec{r}, t)$ when transforming between gauges.

Derived last time

$$\vec{\nabla}^2\chi - \mu_0\epsilon_0\frac{\partial^2\chi}{\partial t^2} = 0 \tag{37.15}$$

is the *constraint on gauge transformation*.

Work in the Lorentz gauge.

Free electromagnetic field, no currents, no magnetic monopoles.

Solve wave equation 1

$$\vec{\nabla}^2\vec{A} - \mu_0\epsilon_0\frac{\partial^2\vec{A}}{\partial t^2} = 0$$

$$\vec{\nabla}^2\vec{A} - \frac{1}{c^2}\frac{\partial^2\vec{A}}{\partial t^2} = 0 \tag{37.16}$$

where $c^2 = \frac{1}{\mu_0\epsilon_0}$.

General solution

$$\vec{A} = \vec{A_0}\cos(\omega t - \vec{k}\cdot\vec{r} + \phi_p) \tag{37.17}$$

Since $\vec{E} = -\vec{\nabla}\phi - \frac{\partial\vec{A}}{\partial t}$ and we assume a constant scalar potential ϕ

$$\vec{E} = -\frac{\partial\vec{A}}{\partial t}$$

$$\vec{E} = \omega \vec{A}_0 \sin(\omega t - \vec{k} \cdot \vec{r} + \phi_p) \tag{37.18}$$

Since $\vec{\nabla} \cdot \vec{A} = 0$ from Lorentz condition and the assumption of a constant scalar potential

$$\vec{k} \cdot \vec{A}_0 \sin(\omega t - \vec{k} \cdot \vec{r} + \phi_p) = 0 \tag{37.19}$$

and $\vec{k} \cdot \vec{A}_0 = 0$ for this to be true.

Since $\vec{B} = \vec{\nabla} \times \vec{A}$ from beginning of section

$$\vec{B} = -(\vec{k} \times \vec{A}_0) \sin(\omega t - \vec{k} \cdot \vec{r} + \phi_p) = 0 \tag{37.20}$$

So $\vec{B}$ is $\perp$ to both $\vec{k}$ and $\vec{A}_0$.

Again,

$$\begin{aligned} &\vec{B} \perp \vec{E} \\ &\vec{B} \perp \vec{A} \\ &\vec{B} \perp \vec{k} \qquad \text{etc} \end{aligned}$$

$\vec{E}$, $\vec{B}$ same frequency and have same phase. Also mention that

$$\vec{E}_0 = -\omega \vec{A}_0$$

Chapter 38

Hamiltonian derived from the Lorentz Force

The Lorentz force on a particle with charge q is defined as

$$\vec{F} = q(\vec{E} + \vec{v} \times \vec{B}) \tag{38.1}$$

(Force on a charged particle in the presence of electric and magnetic fields)

From Newton's equation of motion $\vec{F} = m\vec{a}$ or $m\vec{r''}$. Therefore,

$$m\vec{r''} = q(\vec{E} + \vec{v} \times \vec{B})$$

To keep things simple, just take the x component.

$$mx'' = q(E_x + y'B_z - z'B_y) \tag{38.2}$$

We got this term from

$$\vec{v} \times \vec{B} = \begin{vmatrix} \vec{i} & \vec{j} & \vec{k} \\ x' & y' & z' \\ B_x & B_y & B_z \end{vmatrix}$$

where the x component is $\vec{i}(y'B_z - z'B_y)$, x component of curl.

Now if you look at the above expression you see that we are going to need a more explicit form for E_x and for B_Z and B_y. We get these more explicit expressions from the Maxwell relations we derived earlier.

$$\vec{E} = -\vec{\nabla}\phi - \frac{\partial \vec{A}}{\partial t} \tag{38.3}$$

$$\vec{B} = \vec{\nabla} \times \vec{A} \tag{38.4}$$

From the first expression we get

$$E_x = -\frac{\partial \phi}{\partial x} - \frac{\partial A_x}{\partial t} \tag{38.5}$$

From the second expression $\vec{\nabla} \times \vec{A} = \vec{B}$

$$\begin{vmatrix} \vec{i} & \vec{j} & \vec{k} \\ \frac{\partial}{\partial x} & \frac{\partial}{\partial y} & \frac{\partial}{\partial z}' \\ A_x & A_y & A_z \end{vmatrix}$$

$$B_y = -\left(\frac{\partial A_z}{\partial x} - \frac{\partial A_x}{\partial z}\right) \tag{38.6}$$

$$B_z = \left(\frac{\partial A_y}{\partial x} - \frac{\partial A_x}{\partial y}\right) \tag{38.7}$$

This gives us

$$mx'' = q\left[\left(-\frac{\partial \phi}{\partial x} - \frac{\partial A_x}{\partial t}\right) + y'\left(\frac{\partial A_y}{\partial x} - \frac{\partial A_x}{\partial y}\right) + z'\left(\frac{\partial A_z}{\partial x} - \frac{\partial A_x}{\partial z}\right)\right] \tag{38.8}$$

Now at this point we want to find a Lagrangian that is consistent with the above Lorentz force.

We try

$$L = \frac{1}{2}mr'^2 + q\vec{r'} \cdot \vec{A} - q\phi \tag{38.9}$$

Since from the Lagrangian we will find the Hamiltonian of the problem.

The Lagrangian equation of motion is

$$\frac{d}{dt}\frac{\partial L}{\partial q_i'} - \frac{\partial L}{\partial q_i} = 0 \tag{38.10}$$

where q is a coordinate like x, y or z.

Note that $\frac{d}{dt}$ here in Lagrangian mechanics denotes the "total time-derivative". It is defined as

$$\frac{d}{dt} = \frac{\partial}{\partial t} + \sum_{i=1}^{N} q_i' \frac{\partial}{\partial q_i} + \sum_{i=1}^{N} q_i'' \frac{\partial}{\partial q_i'} = 0 \tag{38.11}$$

Now it is apparent that to evaluate the Lagrange equation of motion with our assumed Lagrangian we need $\frac{\partial L}{\partial x'}$ and $\frac{\partial L}{\partial x}$.

Calculate $\frac{\partial L}{\partial x'}$

$$\frac{\partial L}{\partial x'} = \frac{1}{2} m 2x' + qA_x = mx' + qA_x \tag{38.12}$$

Calculate $\frac{\partial L}{\partial x}$

$$\frac{\partial L}{\partial x} = qr' \frac{\partial A}{\partial x} - q\frac{\partial \phi}{\partial x} \tag{38.13}$$

Now replace the above two expressions into the Lagrange equation of motion and see what we get.

$$\frac{d}{dt}\left(mx' + qA_x\right) - q\vec{r'}\frac{\partial \vec{A}}{\partial x} + q\frac{\partial \phi}{\partial x} = 0$$

$$mx'' + q\frac{dA_x}{dt} - q\left(x', y', z'\right) \cdot \left(\frac{\partial A_x}{\partial x}, \frac{\partial A_y}{\partial x}, \frac{\partial A_z}{\partial x}\right) + q\frac{\partial \phi}{\partial x} = 0$$

Recall that we are dealing with the total time derivative.

$$mx'' + q\frac{dA_x}{dt} - q\left(x'\frac{\partial A_x}{\partial x} + y'\frac{\partial A_y}{\partial x} + z'\frac{\partial A_z}{\partial x}\right) + q\frac{\partial \phi}{\partial x} = 0 \tag{38.14}$$

The total time derivative is defined as

$$\frac{dF(t, \vec{r}, \vec{r'})}{dt} = \frac{\partial F}{\partial t} + \sum_{i=1}^{N} r_i' \frac{\partial F}{\partial r_i} + \sum_{i=1}^{N} r_i'' \frac{\partial F}{\partial q_i'} = 0$$

So

$$q\frac{dA_x}{dt} = q\left[\frac{\partial A_x}{\partial t} + x'\frac{\partial A_x}{\partial x} + y'\frac{\partial A_x}{\partial y} + z'\frac{\partial A_x}{\partial z}\right] \tag{38.15}$$

No other terms since $\vec{A}$ is a function of $\vec{r}$, t. Replace this into our original expression to get

$$mx'' + q\left(\frac{\partial A_x}{\partial t} + x'\frac{\partial A_x}{\partial x} + y'\frac{\partial A_x}{\partial y} + z'\frac{\partial A_x}{\partial z}\right) - q\left(x'\frac{\partial A_x}{\partial x} + y'\frac{\partial A_y}{\partial x} + z'\frac{\partial A_z}{\partial x}\right) + q\frac{\partial \phi}{\partial x} = 0$$

$$mx'' + q\frac{\partial A_x}{\partial t} + q\left(x'\frac{\partial A_x}{\partial x} + y'\frac{\partial A_x}{\partial y} + z'\frac{\partial A_x}{\partial z}\right) - q\left(x'\frac{\partial A_x}{\partial x} + y'\frac{\partial A_y}{\partial x} + z'\frac{\partial A_z}{\partial x}\right) + q\frac{\partial \phi}{\partial x} = 0$$

$$mx'' + q\frac{\partial A_x}{\partial t} + q\left[y'\left(\frac{\partial A_x}{\partial y} - \frac{\partial A_y}{\partial x}\right) + z'\left(\frac{\partial A_x}{\partial z} - \frac{\partial A_z}{\partial x}\right)\right] + q\frac{\partial \phi}{\partial x} = 0$$

$$mx'' + q\left(\frac{\partial A_x}{\partial t} + \frac{\partial \phi}{\partial x}\right) + q\left[y'\left(\frac{\partial A_x}{\partial y} - \frac{\partial A_y}{\partial x}\right) + z'\left(\frac{\partial A_x}{\partial z} - \frac{\partial A_z}{\partial x}\right)\right] = 0$$

$$mx'' + q\left[\left(\frac{\partial A_x}{\partial t} + \frac{\partial \phi}{\partial x}\right) + y'\left(\frac{\partial A_x}{\partial y} - \frac{\partial A_y}{\partial x}\right) + z'\left(\frac{\partial A_x}{\partial z} - \frac{\partial A_z}{\partial x}\right)\right] = 0$$

$$mx'' = q\left[\left(-\frac{\partial A_x}{\partial t} - \frac{\partial \phi}{\partial x}\right) + y'\left(\frac{\partial A_y}{\partial x} - \frac{\partial A_x}{\partial y}\right) + z'\left(\frac{\partial A_z}{\partial x} - \frac{\partial A_x}{\partial z}\right)\right] \tag{38.16}$$

This expression is *identical* to the Lorentz Force and shows that our choice of Lagrangian was appropriate.

Now that our Lagrangian is deemed good, we can go and find our desired classical Hamiltonian through

$$H = \vec{p}\cdot\vec{r'} - L \tag{38.17}$$

where $\vec{p}$ is called the conjugate momentum.

$$L = \frac{1}{2}m\vec{r'}^2 + q\vec{r'}\cdot\vec{A} - q\phi \tag{38.18}$$

The conjugate momentum is

$$p_i = \frac{\partial L}{\partial r'_i} \tag{38.19}$$

or alternatively

$$\vec{p} = \frac{\partial L}{\partial \vec{r'}} \tag{38.20}$$

$$\vec{p} = m\vec{r'} + q\vec{A} \tag{38.21}$$

and conversely

$$\vec{r'} = \left(\frac{\vec{p} - q\vec{A}}{m}\right) \tag{38.22}$$

(we will use this expression)

The classical Hamiltonian is

$$\begin{aligned}
H &= \vec{p}\cdot\vec{r'} - L \\
&= \vec{p}\cdot\vec{r'} - \frac{1}{2}m\vec{r'}^2 - q\vec{r'}\cdot\vec{A} + q\phi \\
&= \vec{p}\cdot\left(\frac{\vec{p}-q\vec{A}}{m}\right) - \frac{m}{2}\frac{1}{m^2}\left(\vec{p}-q\vec{A}\right)^2 - \frac{q}{m}\left(\vec{p}-q\vec{A}\right)\cdot\vec{A} + q\phi \\
&= \frac{\vec{p}\cdot\left(\vec{p}-q\vec{A}\right)}{m} - \frac{\left(\vec{p}-q\vec{A}\right)^2}{2m} - \frac{q\left(\vec{p}-q\vec{A}\right)\cdot\vec{A}}{m} + q\phi \\
&= -\frac{\left(\vec{p}-q\vec{A}\right)^2}{2m} + \frac{\vec{p}\cdot\left(\vec{p}-q\vec{A}\right)}{m} - \frac{q\left(\vec{p}-q\vec{A}\right)\cdot\vec{A}}{m} + q\phi
\end{aligned}$$

But

$$\begin{aligned}
\frac{\vec{p}\cdot\left(\vec{p}-q\vec{A}\right)}{m} - \frac{q\left(\vec{p}-q\vec{A}\right)\cdot\vec{A}}{m} &= \frac{\left(\vec{p}-q\vec{A}\right)\left(\vec{p}-q\vec{A}\right)}{m} \\
&= \frac{\left(\vec{p}-q\vec{A}\right)^2}{m} \\
&= \frac{2\left(\vec{p}-q\vec{A}\right)^2}{2m}
\end{aligned}$$

So

$$\begin{aligned}
H &= -\frac{\left(\vec{p}-q\vec{A}\right)^2}{2m} + \frac{2\left(\vec{p}-q\vec{A}\right)^2}{2m} + q\phi \\
&= \frac{\left(\vec{p}-q\vec{A}\right)^2}{2m} + q\phi
\end{aligned}$$

$$\boxed{H = \frac{\left(\vec{p}-q\vec{A}\right)^2}{2m} + q\phi} \qquad (38.23)$$

Desired classical Hamiltonian.

In general one can add any other potential V to H

$$H = \frac{\left(\vec{p}-q\vec{A}\right)^2}{2m} + q\phi + V \qquad \text{General expression} \qquad (38.24)$$

The classical Hamiltonian uses the vector potential $\vec{A}$ and the scalar potential ϕ rather than $\vec{E}$ and $\vec{B}$ directly.

Expand the squared term

$$\left(\vec{p} - q\vec{A}\right) \cdot \left(\vec{p} - q\vec{A}\right) = \vec{p}^2 + q^2\vec{A}^2 - q\vec{p} \cdot \vec{A} - q\vec{A} \cdot \vec{p}$$

$$H = \frac{1}{2m}\left(\vec{p}^2 + q^2\vec{A}^2 - q\left(\vec{p} \cdot A + \vec{A} \cdot \vec{p}\right)\right) + q\phi + V$$

$$H = \left(\frac{\vec{p}^2}{2m} + q\phi + V\right) + \frac{q^2\vec{A}^2}{2m} - \frac{q}{2m}\left(\vec{p} \cdot \vec{A} + \vec{A} \cdot \vec{p}\right)$$

Let's simplify this a little more by first noting that in the Coulomb gauge $\phi = 0$. Next note that the $\frac{q^2\vec{A}^2}{2m}$ term is important only at high powers. Since we generally deal with the low power linear spectroscopy regime we can drop this term as well.

$$H = \left(\frac{\vec{p}^2}{2m} + V\right) - \frac{q}{2m}\left(\vec{p} \cdot \vec{A} + \vec{A} \cdot \vec{p}\right)$$

Now in general $\vec{p} \cdot \vec{A} \neq \vec{A} \cdot \vec{p}$ but in the Coulomb gauge $\vec{p} \cdot \vec{A} = \vec{A} \cdot \vec{p}$.

Proof:

Use $\vec{p} = -i\hbar\nabla \Rightarrow \vec{p} \cdot \vec{A} = -i\hbar\nabla \cdot \vec{A}$. Use a test wavefunction ψ

$$\begin{aligned}\left(\vec{p} \cdot \vec{A}\right)\psi = \left(-i\hbar\nabla \cdot \vec{A}\right)\psi = -i\hbar\nabla \cdot \left(\vec{A}\psi\right) &= -i\hbar\left[\vec{A} \cdot \nabla\psi + \psi\nabla \cdot \vec{A}\right] \\ = -i\hbar\left[\vec{A} \cdot \nabla\psi + \nabla \cdot \vec{A}\psi\right] &= -i\hbar\left[\vec{A} \cdot \nabla + \nabla \cdot \vec{A}\right]\psi\end{aligned}$$

Now remove ψ (our test wavefunction)

$$\vec{p} \cdot \vec{A} = -i\hbar\left[\vec{A} \cdot \nabla + \nabla \cdot \vec{A}\right]\psi$$

but we know from our previous work on Maxwell's equations that $\vec{\nabla} \cdot \vec{A} = -\mu_0\epsilon_0\frac{\partial\phi}{\partial t}$ and $\phi = 0$, $\Rightarrow \vec{\nabla} \cdot \vec{A} = 0$.

$$\vec{p} \cdot \vec{A} = -i\hbar\vec{A} \cdot \nabla = \vec{A} \cdot \vec{p}$$

$$\vec{p} \cdot \vec{A} = \vec{A} \cdot \vec{p}$$

This leaves us with

$$H = \left(\frac{\vec{p}^2}{2m} + V \right) - \frac{q \left(\vec{p} \cdot \vec{A} \right)}{m} \tag{38.25}$$

Our desired final expression for the Hamiltonian.

Perhaps more relevantly $p \rightarrow -i\hbar\nabla$

$$H = \left(-\frac{\hbar^2 \vec{\nabla}^2}{2m} + V \right) - \frac{q \left(\vec{A} \cdot \vec{P} \right)}{m} \tag{38.26}$$

$$H = H^{(0)} + H^{(1)}$$

This should look familiar now.

Chapter 39

Interlude

Ok, so now you're wondering-great we went though all this work to obtain a new Hamiltonian which ultimately describes the interaction of light and matter. But didn't we use another form of the Hamiltonian before?

$$\begin{aligned} H &= -\frac{\hbar^2\nabla^2}{2m} + V - \frac{q}{m}(A \cdot P) \\ H^{(1)} &= -\frac{q}{m}(A \cdot P) \end{aligned}$$

versus

$$\begin{aligned} H &= -\frac{\hbar^2\nabla^2}{2m} + V - \mu \cdot \epsilon \\ H^{(1)} &= -\mu \cdot \epsilon \end{aligned}$$

Are they the same thing?

Recall that from Maxwell's equation we found that

$$A = A_0 cos(\omega t - k \cdot r + \phi_P)$$

For convenience we will drop the phase and note that $A_0 = A_0\hat{e}$ where $\hat{e}$ is a unit vector and A_0 is a scalar amplitude.

$$A = A_0\hat{e}cos(\omega t - k \cdot r)$$

Now recall that $\epsilon = -\frac{\partial A}{\partial t}$

$$\epsilon = \omega A_0\hat{e}sin(\omega t - k \cdot r)$$

Consider our original version of the perturbation Hamiltonian ($H^{(1)} = -\mu \cdot \epsilon$).

$$\begin{aligned} H^{(1)} &= -\mu \cdot \omega A_0 \hat{e} sin(\omega t - k \cdot r) \\ &= -(\mu \cdot \hat{e}) \omega A_0 sin(\omega t - k \cdot r) \\ &= -\omega A_0 (\mu \cdot \hat{e}) \left(\frac{e^{i\omega t} e^{-ik\cdot r} - e^{-i\omega t} e^{ik\cdot r}}{2i} \right) \end{aligned}$$

We invoke what is called the electric dipole approximation where $e^{ik\cdot r} \simeq 1$.

$$H^{(1)} = -\omega A_0 (\mu \cdot \hat{e}) \left(\frac{e^{i\omega t} - e^{-i\omega t}}{2i} \right)$$

If we choose the z component we get

$$H^{(1)} = -\omega A_0 \mu_z \left(\frac{e^{i\omega t} - e^{-i\omega t}}{2i} \right)$$

If you look carefully you will recognize that our old ϵ_0 term is here

$$\epsilon_0 = \omega A_0$$

$$H^{(1)} = -\epsilon_0 \mu_z \left(\frac{e^{i\omega t} - e^{-i\omega t}}{2i} \right)$$

Sandwich this term between some test initial and final state

$$< k|H^{(1)}|n >= -\epsilon_0 \left(\frac{e^{i\omega t} - e^{-i\omega t}}{2i} \right) < k|\mu_z|n >$$

$$\boxed{< k|H^{(1)}|n >= -\frac{\epsilon_0 < k|\mu_z|n >}{2i} (e^{i\omega t} - e^{-i\omega t})} \tag{39.1}$$

Now consider our second more recent version of the perturbation Hamiltonian ($H^{(1)} = -\frac{q}{m} A \cdot P$) where $A = A_0 \hat{e} cos(\omega t - k \cdot r)$

$$\begin{aligned} H^{(1)} &= -\frac{q}{m} A_0 \hat{e} cos(\omega t - k \cdot r) \cdot P \\ &= -\frac{q}{m} A_0 \left(\frac{e^{i\omega t} e^{-ik\cdot r} + e^{-i\omega t} e^{ik\cdot r}}{2} \right) (\hat{e} \cdot P) \end{aligned}$$

Again take the electric dipole approximation $e^{ik\cdot r} \simeq 1$

$$H^{(1)} = -\frac{qA_0}{m} \left(\frac{e^{i\omega t} + e^{-i\omega t}}{2} \right) (\hat{e} \cdot P)$$

Now sandwich this between some test initial and final states

$$< k|H^{(1)}|n >= -\frac{qA_0}{m}\left(\frac{e^{i\omega t}+e^{-i\omega t}}{2}\right) < k|\hat{e}\cdot P|n >$$

where now we recognize that

$$\boxed{P = \tfrac{im}{\hbar}[H^{(0)}, r]} \tag{39.2}$$

Proof:

$$\frac{im}{\hbar}[H^{(0)}, r] = \frac{im}{\hbar}[\frac{P^2}{2m}, r] = \frac{i}{2\hbar}[P^2, r]$$

Now use a commutator relation we learned a long time ago

$$[AB, C] = A[B, C] + [A, C]B$$

$$[P^2, r] = P[P, r] + [P, r]P$$

where recall that $[P, r] = -i\hbar$. Therefore

$$\begin{aligned}\frac{i}{2\hbar}[P^2, r] &= \frac{i}{2\hbar}[P(-i\hbar) + (-i\hbar)P] \\ &= \frac{i(-i\hbar)2P}{2\hbar} \\ &= P\end{aligned}$$

Therefore

$$P = \frac{im}{\hbar}[H^{(0)}, r]$$

End of proof.

So back to our original expression

$$\begin{aligned}
< k|H^{(1)}|n > &= -\frac{qA_0}{m}\left(\frac{e^{i\omega t}+e^{-i\omega t}}{2}\right)\hat{e}\cdot < k|P|n > \\
&= -\frac{qA_0}{m}\left(\frac{e^{i\omega t}+e^{-i\omega t}}{2}\right)\hat{e}\cdot < k|\frac{im}{\hbar}[H^{(0)},r]|n > \\
&= -\frac{qA_0}{m}\frac{im}{\hbar}\left(\frac{e^{i\omega t}+e^{-i\omega t}}{2}\right)\hat{e}\cdot < k|[H^{(0)},r]|n > \\
&= -\frac{qA_0 i}{\hbar}\left(\frac{e^{i\omega t}+e^{-i\omega t}}{2}\right)\hat{e}\cdot < k|H^{(0)}r - rH^{(0)}|n > \\
&= -\frac{qA_0 i}{\hbar}\left(\frac{e^{i\omega t}+e^{-i\omega t}}{2}\right)\hat{e}\cdot\left[< k|H^{(0)}r|n > - < k|rH^{(0)}|n >\right] \\
&= -\frac{qA_0 i}{\hbar}\left(\frac{e^{i\omega t}+e^{-i\omega t}}{2}\right)\hat{e}\cdot\left[\epsilon_k < k|r|n > -\epsilon_n < k|r|n >\right] \\
&= -\frac{qA_0 i}{\hbar}\left(\frac{e^{i\omega t}+e^{-i\omega t}}{2}\right)(\epsilon_k-\epsilon_n)\hat{e}\cdot < k|r|n > \\
&= -A_0\omega_{kn} i\left(\frac{e^{i\omega t}+e^{-i\omega t}}{2}\right)\hat{e}\cdot < k|qr|n >
\end{aligned}$$

where $\omega_{kn} = \frac{\epsilon_k-\epsilon_n}{\hbar} = \omega$. Now recall that $\mu = qr$. We then have

$$\begin{aligned}
&= -A_0\omega i\left(\frac{e^{i\omega t}+e^{-i\omega t}}{2}\right)\hat{e}\cdot < k|\mu|n > \\
&= -A_0\omega i\left(\frac{e^{i\omega t}+e^{-i\omega t}}{2}\right) < k|\hat{e}\cdot\mu|n >
\end{aligned}$$

Now if we choose the z component we get

$$= -A_0\omega i\left(\frac{e^{i\omega t}+e^{-i\omega t}}{2}\right) < k|\mu_z|n >$$

Now recall that $\epsilon_0 = A_0\omega$ giving

$$\begin{aligned}
&= -\epsilon_0 i\left(\frac{e^{i\omega t}+e^{-i\omega t}}{2}\right) < k|\mu_z|n > \\
&= \epsilon_0\left(\frac{e^{i\omega t}+e^{-i\omega t}}{2i}\right) < k|\mu_z|n >
\end{aligned}$$

Therefore

$$\boxed{< k|H^{(1)}|n >= \frac{\epsilon_0 < k|\mu_z|n >}{2i}(e^{i\omega t}+e^{-i\omega t})} \qquad (39.3)$$

Summary

Case 1, starting with $H^{(1)} = -\mu \cdot \epsilon$

$$\boxed{< k|H^{(1)}|n >= -\frac{\epsilon_0 < k|\mu_z|n >}{2i}(e^{i\omega t} - e^{-i\omega t})} \qquad (39.4)$$

Case 2, starting with $H^{(1)} = -\frac{q}{m} A \cdot P$

$$\boxed{< k|H^{(1)}|n >= \frac{\epsilon_0 < k|\mu_z|n >}{2i}(e^{i\omega t} + e^{-i\omega t})} \qquad (39.5)$$

Notice that the two expressions are identical if we take the Rotating Wave Approximation and drop the 2nd term $e^{-i\omega t}$. So you see the $H^{(1)} = -\mu \cdot \epsilon$ approach is just a shortcut to speed things up.

Chapter 40

The electric dipole approximation and A_0

Recall from our interlude where we showed $H^{(1)} = -\mu\cdot\epsilon$ and $H^{(1)} = -\frac{q}{m}A\cdot P$ were equivalent we had $\epsilon \propto sin(\omega t - k\cdot r)$ and we applied a Euler relation to get

$$\begin{aligned} \epsilon &\propto \left(\frac{e^{i(\omega t - k\cdot r)} - e^{-i(\omega t - k\cdot r)}}{2i}\right) \\ &\propto \left(\frac{e^{i\omega t}e^{-ik\cdot r} - e^{-i\omega t}e^{ik\cdot r}}{2i}\right) \end{aligned}$$

Now here we invoked what is commonly called the electric dipole approximation

$$\begin{aligned} e^{ik\cdot r} &\simeq 1 \\ &\text{or} \\ e^{-ik\cdot r} &\simeq 1 \end{aligned}$$

This Taylor series approximation is valid if $(k\cdot r)$ is small.

To show that this is valid, take r of molecular dimensions and $k = \frac{2\pi}{\lambda}$ where λ is the wavelength of visible light. Here assume $r = 50\mathring{A}$ and $k = \frac{2\pi}{\lambda} = \frac{2\pi}{5x10^3\mathring{A}}$ (500 nm light).

$$kr = 50\left(\frac{2\pi}{5000}\right) = 0.0628$$

So $k\cdot r$ is small and the Taylor series approximation is valid.

Now let's take another aside to find out a more explicit form for A_0 (as in $A = A_0 cos(\omega t - k \cdot r)$) where $A_0 = A_0 \hat{e}$ and $\hat{e}$ is a unit vector.

Ok, the quantity A_0 is related to the energy density of the field.

Picture a volume V and the time average $E = N\hbar\omega$ where N is the total number of photons with individual energy $\hbar\omega$.

$$E = N\hbar\omega = \int d^3r < \text{energy density} >$$

where the energy density defined in SI units is

$$\boxed{U = \frac{\epsilon_0 |E|^2 + \frac{1}{\mu_0}|B|^2}{2}} \tag{40.1}$$

We have expressions for both E and B from our work on Maxwell's equations.

$$\begin{aligned} A &= A_0 \hat{e} cos(\omega t - k \cdot r) \\ E &= \omega A_0 \hat{e} sin(\omega t - k \cdot r) \\ B &= -(k \times \hat{e}) A_0 sin(\omega t - k \cdot r) \end{aligned}$$

Note that we have dropped the phase factor ϕ_p.

To be further useful let $k = kn$ where n is a unit vector and $k = \frac{\omega}{c}$.

This leads to

$$B = -k(n \times \hat{e}) A_0 sin(\omega t - k \cdot r)$$

$$\boxed{B = -\frac{A_0 \omega}{c}(n \times \hat{e}) sin(\omega t - k \cdot r)} \tag{40.2}$$

Now using these expressions for E and B we solve for the energy density and in turn get the average energy density. Just do $\frac{1}{\mu_0}|B|^2$ and we will find that it is actually equivalent to $\epsilon_0 |E|^2$.

$$\begin{aligned} |B|^2 &= \frac{A_0^2 \omega^2}{c^2}(n \times \hat{e})^2 sin^2(\omega t - k \cdot r) \\ \frac{1}{\mu_0} &= \epsilon_0 c^2 \end{aligned}$$

since

$$\boxed{\epsilon_0 \mu_0 = \frac{1}{c^2}} \tag{40.3}$$

Putting it all together

$$\frac{1}{\mu}|B|^2 = (\epsilon_0 c^2)\frac{A_0^2\omega^2}{c^2}(n \times \hat{e})^2 sin^2(\omega t - k \cdot r)$$

$$\boxed{\tfrac{1}{\mu}|B|^2 = \epsilon_0 A_0^2\omega^2(n \times \hat{e})^2 sin^2(\omega t - k \cdot r)} \tag{40.4}$$

By inspection $\frac{1}{\mu}|B|^2 = \epsilon_0|E|^2$ and as a consequence

$$\boxed{U = \epsilon_0|E|^2} \tag{40.5}$$

Now we want $\bar{U}_{avg} = \epsilon_0\omega^2 A_0^2 < sin^2(\omega t - k \cdot r) >$ but we know that the average value of $sin^2 x = \frac{1}{2}$ therefore

$$\boxed{\bar{U}_{avg} = \tfrac{\epsilon_0\omega^2 A_0^2}{2}} \tag{40.6}$$

This is the average value of the energy density.

Now back to E_{tot}.

$$\begin{aligned} E_{tot} = N\hbar\omega &= \int d^3r \left(\frac{\epsilon_0\omega^2 A_0^2}{2}\right) \\ &= \frac{\epsilon_0\omega^2 A_0^2}{2}\int d^3r \\ &= \frac{\epsilon_0\omega^2 A_0^2 V}{2} \end{aligned}$$

where V is a unit volume.

$$\begin{aligned} A_0^2 &= \frac{2N\hbar\omega}{\epsilon_0\omega^2 V} = \frac{2N\hbar}{\epsilon_0\omega V} \\ A_0 &= \sqrt{\frac{2N\hbar}{\epsilon_0\omega V}} \\ &= \sqrt{\frac{2\hbar}{\epsilon_0\omega}\left(\frac{N}{V}\right)} \end{aligned}$$

$$\boxed{A_0 = \sqrt{\tfrac{2\hbar}{\epsilon_0\omega}\left(\tfrac{N}{V}\right)}} \tag{40.7}$$

alternatively

$$\boxed{A_0 = \sqrt{\tfrac{h}{2\pi^2\epsilon_0 V}\left(\tfrac{N}{V}\right)}} \tag{40.8}$$

in SI units.

Chapter 41

More electric dipole stuff

We know that

$$\begin{aligned} H^{(1)} &= -\mu \cdot \epsilon \\ \text{and} & \\ H^{(1)} &= -\frac{q}{m} A \cdot P \end{aligned}$$

are basically equivalent, where

$$A = A_0 \hat{e} cos(\omega t - k \cdot r)$$

ignoring the phase ϕ_P and

$$\begin{aligned} A_0 &= \sqrt{\frac{2\hbar}{\epsilon_0 \omega}\left(\frac{N}{V}\right)} \\ &= \sqrt{\frac{h}{2\pi^2 \epsilon_0 \nu}\left(\frac{N}{V}\right)} \end{aligned}$$

Now we will rederive our transition probabilities using this second form of the perturbation Hamiltonian with the explicit form of A_0. From before, in the interaction representation and 1st order time dependent perturbation theory, we have

$$P_k = \frac{1}{\hbar^2}\left|\int_{t_0}^{t} dt' e^{i\omega_{kn}t'} < k|H^{(1)}|n >\right|$$

where k is the final state and n is the initial state and $\omega_{kn} = \frac{\epsilon_k - \epsilon_n}{\hbar}$.

Rather than shove into this the following

- a) $H^{(1)}$ is constant
- b) $H^{(1)} \propto sin\omega t$
- c) $H^{(1)} \propto cos\omega t$

like we have done before we will put in $H^{(1)} = -\frac{q}{m}A \cdot P$.

$$\begin{aligned} P_k &= \frac{1}{\hbar^2}\left|\int_{t_0}^{t} dt^{'} e^{i\omega_{kn}t^{'}} < k| - \frac{q}{m}A \cdot P|n >\right|^2 \\ &= \frac{1}{\hbar^2}\left|\int_{t_0}^{t} dt^{'} (-\frac{q}{m}) e^{i\omega_{kn}t^{'}} < k|A \cdot P|n >\right|^2 \end{aligned}$$

where $A = A_0 \hat{e} cos(\omega t - k \cdot r)$.

$$= \frac{1}{\hbar^2}\left|\int_{t_0}^{t} dt^{'} (-\frac{q}{m}) e^{i\omega_{kn}t^{'}} < k|A_0 cos(\omega t - k \cdot r)\hat{e} \cdot P|n >\right|^2$$

Ok, to simplify life we take the electric dipole approximation $e^{ik\cdot r} \simeq 1$ so that $cos(\omega t - k \cdot r) \to cos\omega t$.

$$= \frac{1}{\hbar^2}\left|\int_{t_0}^{t} dt^{'} (-\frac{q}{m}) e^{i\omega_{kn}t^{'}} A_0 cos\omega t < k|\hat{e} \cdot P|n >\right|^2$$

Now recall that $P = \frac{im}{\hbar}[H^{(0)}, r]$ then we get

$$\begin{aligned} &= \frac{1}{\hbar^2}\left|\int_{t_0}^{t} dt^{'} (-\frac{q}{m}) e^{i\omega_{kn}t^{'}} A_0 cos\omega t \hat{e} \cdot < k|P|n >\right|^2 \\ &= \frac{1}{\hbar^2}\left|\int_{t_0}^{t} dt^{'} (-\frac{q}{m}) e^{i\omega_{kn}t^{'}} A_0 cos\omega t \hat{e} \frac{im}{\hbar} < k|[H^{(0)}, r]|n >\right|^2 \end{aligned}$$

The bra-ket stuff simplifies as

$$\begin{aligned} &= < k|H^{(0)}r - rH^{(0)}|n > \\ &= < k|H^{(0)}r|n > - < k|rH^{(0)}|n > \\ &= \epsilon_k < k|r|n > - < k|r|n > \epsilon_n \\ &= (\epsilon_k - \epsilon_n) < k|r|n > \end{aligned}$$

Replacing this back into our original expression we get

$$= \frac{1}{\hbar^2}\left|\int_{t_0}^{t} dt^{'} (-\frac{q}{m}) e^{i\omega_{kn}t^{'}} A_0 cos\omega t im \frac{\epsilon_k - \epsilon_n}{\hbar} \hat{e} \cdot < k|r|n >\right|^2$$

where $\omega_{kn} = \frac{\epsilon_k - \epsilon_n}{\hbar}$

$$= \frac{1}{\hbar^2} \left| \int_{t_0}^{t} dt^{'} (-q) e^{i\omega_{kn}t^{'}} A_0 cos\omega t i\omega_{kn} \hat{e} \cdot < k|r|n > \right|^2$$

Now convert to transition dipole form like we are accustomed to seeing

$$\begin{aligned} &= \frac{1}{\hbar^2} \left| \int_{t_0}^{t} dt^{'} (-i\omega_{kn}) e^{i\omega_{kn}t^{'}} A_0 cos\omega t \hat{e} \cdot < k|qr|n > \right|^2 \\ &= \frac{1}{\hbar^2} \left| \int_{t_0}^{t} dt^{'} (-i\omega_{kn}) e^{i\omega_{kn}t^{'}} A_0 cos\omega t < k|\hat{e} \cdot qr|n > \right|^2 \end{aligned}$$

where $\mu = qr$. Now we get

$$= \frac{1}{\hbar^2} \left| \int_{t_0}^{t} dt^{'} (-i\omega_{kn}) e^{i\omega_{kn}t^{'}} A_0 cos\omega t < k|\hat{e} \cdot \mu|n > \right|^2$$

Take the z component like usual.

$$\begin{aligned} &= \frac{1}{\hbar^2} \left| \int_{t_0}^{t} dt^{'} (-i\omega_{kn}) e^{i\omega_{kn}t^{'}} A_0 cos\omega t < k|\mu_z|n > \right|^2 \\ &= \frac{\omega_{kn}^2 A_0^2 | < k|\mu_z|n > |^2}{\hbar^2} \left| \int_{t_0}^{t} dt^{'} e^{i\omega_{kn}t^{'}} cos\omega t \right|^2 \\ &= \frac{\omega_{kn}^2 A_0^2 | < k|\mu_z|n > |^2}{\hbar^2} \left| \int_{t_0}^{t} dt^{'} e^{i\omega_{kn}t^{'}} \frac{e^{i\omega t} + e^{-i\omega t}}{2} \right|^2 \\ &= \frac{\omega_{kn}^2 A_0^2 | < k|\mu_z|n > |^2}{4\hbar^2} \left| \int_{t_0}^{t} dt^{'} (e^{i(\omega_{kn}+\omega)t^{'}} + e^{i(\omega_{kn}-\omega)t^{'}}) \right|^2 \end{aligned}$$

Ok, at this point you realize that you can simplify life by looking at either the resonant or non-resonant terms separately. Then its just an integral over 1 term.

However if you want to brute force this integral you can go ahead and do it. Just drop the cross terms because they turn out to be small.

You basically get (consider the integral separately for notational convenience)

$$\left. \frac{e^{i(\omega_{kn}+\omega)t^{'}}}{i(\omega_{kn}+\omega)} \right|_{t_0}^{t} + \left. \frac{e^{i(\omega_{kn}-\omega)t^{'}}}{i(\omega_{kn}-\omega)} \right|_{t_0}^{t}$$

now if $t_0 = 0$ we get

$$\frac{e^{i(\omega_{kn}+\omega)t}-1}{i(\omega_{kn}+\omega)}+\frac{e^{i(\omega_{kn}-\omega)t}-1}{i(\omega_{kn}-\omega)}$$

In each case just like we've done many times in the past, extract out $e^{\frac{i(\omega_{kn}+\omega)t}{2}}$ or $e^{\frac{i(\omega_{kn}-\omega)t}{2}}$. We then get

$$\begin{aligned}
&= e^{\frac{i(\omega_{kn}+\omega)t}{2}}\left(\frac{e^{i(\omega_{kn}+\omega)t}-e^{-i(\omega_{kn}+\omega)t}}{i(\omega_{kn}+\omega)}\right)\\
&+ e^{\frac{i(\omega_{kn}-\omega)t}{2}}\left(\frac{e^{\frac{i(\omega_{kn}-\omega)t}{2}}-e^{\frac{-i(\omega_{kn}-\omega)t}{2}}}{i(\omega_{kn}-\omega)}\right)\\
&= \frac{2e^{\frac{i(\omega_{kn}+\omega)t}{2}}}{(\omega_{kn}+\omega)}\left(\frac{e^{i(\omega_{kn}+\omega)t}-e^{-i(\omega_{kn}+\omega)t}}{2i}\right)\\
&+ \frac{2e^{\frac{i(\omega_{kn}-\omega)t}{2}}}{(\omega_{kn}-\omega)}\left(\frac{e^{\frac{i(\omega_{kn}-\omega)t}{2}}-e^{\frac{-i(\omega_{kn}-\omega)t}{2}}}{2i}\right)\\
&= \frac{2e^{\frac{i(\omega_{kn}+\omega)t}{2}}}{(\omega_{kn}+\omega)}sin(\frac{(\omega_{kn}+\omega)t}{2})+\frac{2e^{\frac{i(\omega_{kn}-\omega)t}{2}}}{(\omega_{kn}-\omega)}sin(\frac{(\omega_{kn}-\omega)t}{2})
\end{aligned}$$

Now we square this expression and drop any cross terms.

$$\begin{aligned}
|\ |^2 &\simeq \frac{4}{(\omega_{kn}+\omega)^2}sin^2(\frac{(\omega_{kn}+\omega)t}{2})+\frac{4}{(\omega_{kn}-\omega)^2}sin^2(\frac{(\omega_{kn}-\omega)t}{2})\\
P_k &\simeq \frac{\omega_{kn}^2 A_0^2| < k|\mu_z|n > |^2}{4\hbar^2}\\
&\left(\frac{4}{(\omega_{kn}+\omega)^2}sin^2(\frac{(\omega_{kn}+\omega)t}{2})+\frac{4}{(\omega_{kn}-\omega)^2}sin^2(\frac{(\omega_{kn}-\omega)t}{2})\right)\\
&\simeq \frac{\omega_{kn}^2 A_0^2| < k|\mu_z|n > |^2}{\hbar^2}\left(\frac{sin^2(\frac{(\omega_{kn}+\omega)t}{2})}{(\omega_{kn}+\omega)^2}+\frac{sin^2(\frac{(\omega_{kn}-\omega)t}{2})}{(\omega_{kn}-\omega)^2}\right)
\end{aligned}$$

Since $\omega \to \omega_{kn}$ or $\omega \to -\omega_{kn}$ but not simultaneously we get two transition probabilities.

$$\boxed{P_{k,abs} = \frac{\omega_{kn}^2 A_0^2|<k|\mu_z|n>|^2}{\hbar^2}\frac{sin^2(\frac{(\omega_{kn}+\omega)t}{2})}{(\omega_{kn}+\omega)^2}} \tag{41.1}$$

$$\boxed{P_{k,emm} = \frac{\omega_{kn}^2 A_0^2|<k|\mu_z|n>|^2}{\hbar^2}\frac{sin^2(\frac{(\omega_{kn}-\omega)t}{2})}{(\omega_{kn}-\omega)^2}} \tag{41.2}$$

These are the absorption probability and stimulated emission transition probabilities respectively.

If you wish recall that $\epsilon_0 = \omega A_0$ and you have identical expressions to that derived previously. Note that some texts will show $\epsilon_o = -\omega A_o$. This is because they have defined $A = A_o\hat{e}cos(kr - \omega t)$ as opposed to what we have done which is $A = A_o\hat{e}cos(\omega t - kr)$.

$$\boxed{P_{k,abs} \simeq \frac{\epsilon_0^2|<k|\mu_z|n>|^2}{\hbar^2}\frac{sin^2(\frac{(\omega_{kn}+\omega)t}{2})}{(\omega_{kn}+\omega)^2}} \tag{41.3}$$

$$\boxed{P_{k,emm} \simeq \frac{\epsilon_0^2|<k|\mu_z|n>|^2}{\hbar^2}\frac{sin^2(\frac{(\omega_{kn}-\omega)t}{2})}{(\omega_{kn}-\omega)^2}} \tag{41.4}$$

These expressions are identical to those found previously, starting with $H^{(1)} = -\mu \cdot \epsilon$ instead of $H^{(1)} = -\frac{q}{m}A \cdot P$.

Now since we want to get the transition rate we can integrate this over a distribution of final states. As before consider $\rho(\omega_k)$ constant.

$$\begin{aligned}
P_{k,group-abs} &= \int_{-\infty}^{\infty} \frac{\epsilon_0^2| < k|\mu_z|n > |^2}{\hbar^2}\frac{sin^2(\frac{(\omega_{kn}+\omega)t}{2})}{(\omega_{kn}+\omega)^2}\rho(\omega_k)d\omega_k \\
&= \frac{\epsilon_0^2| < k|\mu_z|n > |^2}{\hbar^2}\rho(\omega_k)\int_{-\infty}^{\infty} \frac{sin^2(\frac{(\omega_{kn}+\omega)t}{2})}{(\omega_{kn}+\omega)^2}d\omega_k
\end{aligned}$$

Let $x = (\omega_k - \omega_n + \omega)$ and $dx = d\omega_k$. The limits of integration stay the same.

$$= \frac{\epsilon_0^2| < k|\mu_z|n > |^2\rho(\omega_k)}{\hbar^2}\int_{-\infty}^{\infty} \frac{sin^2\frac{xt}{2}}{x^2}dx$$

where we know from before or from a table of integrals that

$$\int_{-\infty}^{\infty} \frac{sin^2\frac{xt}{2}}{x^2}dx = \frac{\pi t}{2}$$

We then get

$$\begin{aligned}
&= \frac{\epsilon_0^2| < k|\mu_z|n > |^2\rho(\omega_k)\pi t}{2\hbar^2} \\
&= \frac{\pi\epsilon_0^2| < k|\mu_z|n > |^2\rho(\omega_k)t}{2\hbar^2}
\end{aligned}$$

Now recall that $\rho(\omega_k) = \hbar\rho(\epsilon_k)$ giving

$$= \frac{\pi\epsilon_0^2| < k|\mu_z|n > |^2\rho(\epsilon_k)t}{2\hbar}$$

The total group transition probability is

$$\boxed{P_{k,group-abs} = \tfrac{\pi}{2\hbar}\epsilon_0^2 |<k|\mu_z|n>|^2 \rho(\epsilon_k) t} \tag{41.5}$$

The total transition rate is

$$\boxed{R = \tfrac{dP_{k,group-abs}}{dt} = \tfrac{\pi}{2\hbar}\epsilon_0^2 |<k|\mu_z|n>|^2 \rho(\epsilon_k)} \tag{41.6}$$

This is Fermi's Golden Rule again.

Now let's do the same for $P_{k,group-emm}$ and $R_{k,group-emm}$

$$\begin{aligned} P_{k,group-emm} &= \int_{-\infty}^{\infty} \frac{\epsilon_0^2 |<k|\mu_z|n>|^2}{\hbar^2} \frac{sin^2(\frac{(\omega_{kn}-\omega)t}{2})}{(\omega_{kn}-\omega)^2} \rho(\omega_k) d\omega_k \\ &= \frac{\epsilon_0^2 |<k|\mu_z|n>|^2}{\hbar^2} \rho(\omega_k) \int_{-\infty}^{\infty} \frac{sin^2(\frac{(\omega_{kn}-\omega)t}{2})}{(\omega_{kn}-\omega)^2} d\omega_k \end{aligned}$$

Let $x = (\omega_k - \omega_n - \omega)$ and $dx = d\omega_k$. The limits of integration stay the same and recall from a table of integrals that

$$\int_{-\infty}^{\infty} \frac{sin^2(\frac{xt}{2})}{x^2} dx = \frac{\pi t}{2}$$

We then get

$$\begin{aligned} &= \frac{\epsilon_0 |<k|\mu_z|n>|^2}{\hbar^2} \rho(\omega_k) \frac{\pi t}{2} \\ &= \frac{\pi \epsilon_0^2}{2\hbar^2} |<k|\mu_z|n>|^2 \rho(\omega_k) t \end{aligned}$$

Convert from $\rho(\omega_k) \to \rho(\epsilon_k)$ and $\rho(\omega_k) = \hbar\rho(\epsilon_k)$ to get

$$= \frac{\pi \epsilon_0^2}{2\hbar} |<k|\mu_z|n>|^2 \rho(\epsilon_k) t$$

$$\boxed{P_{k,group-emm} = \tfrac{\pi}{2\hbar}\epsilon_0^2 |<k|\mu_z|n>|^2 \rho(\epsilon_k) t} \tag{41.7}$$

The transition rate can be obtained from this

$$R_{k,group-emm} = \frac{dP_{k,group-emm}}{dt} = \frac{\pi}{2\hbar}\epsilon_0^2 |<k|\mu_z|n>|^2 \rho(\epsilon_k)$$

giving

$$\boxed{R_{k,group-emm} = \tfrac{\pi}{2\hbar}\epsilon_0^2 |<k|\mu_z|n>|^2 \rho(\epsilon_k)} \tag{41.8}$$

This is Fermi's Golden rule again.

Notice again that the rate of absorption and stimulated emission is equal.

Summary

$$\boxed{P_{k,group-emm} = \tfrac{\pi}{2\hbar}\epsilon_0^2| < k|\mu_z|n > |^2\rho(\epsilon_k)t} \tag{41.9}$$

$$\boxed{P_{k,group-abs} = \tfrac{\pi}{2\hbar}\epsilon_0^2| < k|\mu_z|n > |^2\rho(\epsilon_k)t} \tag{41.10}$$

$$\boxed{R = \tfrac{dP_{k,group-abs}}{dt} = \tfrac{\pi}{2\hbar}\epsilon_0^2| < k|\mu_z|n > |^2\rho(\epsilon_k)} \tag{41.11}$$

$$\boxed{R_{k,group-emm} = \tfrac{\pi}{2\hbar}\epsilon_0^2| < k|\mu_z|n > |^2\rho(\epsilon_k)} \tag{41.12}$$

where in all cases $\epsilon_o = \omega A_o$ and $A_0 = \sqrt{\frac{2\hbar}{\epsilon_0\omega}\left(\frac{N}{V}\right)}$. Again recall that some texts have $\epsilon_o = -\omega A_o$ because they define $A = A_o\hat{e}cos(kr - \omega t)$ versus $A = A_o\hat{e}cos(\omega t - kr)$ as we have done.

Alternatively

Alternatively, recall that an alternate $t \to \infty$ expression can be derived. This is done by invoking an alternative definition of the Delta function.

$$\boxed{\delta(x) = lim_{a\to\infty}\tfrac{sin^2(ax)}{\pi a x^2}} \tag{41.13}$$

So starting with

$$P_{k,abs} \simeq \frac{\epsilon_0^2| < k|\mu_z|n > |^2}{\hbar^2}\frac{sin^2(\frac{(\omega_{kn}+\omega)t}{2})}{(\omega_{kn}+\omega)^2}$$

Let $x = (\omega_{kn} + \omega)$ and $a = \frac{t}{2}$

$$\frac{sin^2(\frac{xt}{2})}{x^2} = \pi a\delta(x) = \frac{\pi t}{2}\delta(\omega_{kn} + \omega)$$

$$\begin{aligned} P_{k,abs} &\simeq \frac{\epsilon_0^2| < k|\mu_z|n > |^2}{\hbar^2}\frac{\pi t}{2}\delta(\omega_{kn} + \omega) \\ &\simeq \frac{\pi}{2\hbar^2}\epsilon_0^2| < k|\mu_z|n > |^2\delta(\omega_{kn} + \omega)t \end{aligned}$$

where $\delta(\omega_{kn} + \omega) = \hbar\delta(\epsilon_{kn} + \epsilon)$. Our desired $t \to \infty$ transition probability is therefore

$$\boxed{P_{k,abs} = \tfrac{\pi}{2\hbar}\epsilon_0^2| < k|\mu_z|n > |^2\delta(\epsilon_{kn} + \epsilon)t} \tag{41.14}$$

The transition rate is

$$R = \frac{dP_{k,abs}}{dt}$$

$$\boxed{R_{k,abs} = \tfrac{\pi}{2\hbar}\epsilon_0^2| < k|\mu_z| > n|^2\delta(\epsilon_{kn} + \epsilon)} \tag{41.15}$$

This is the desired transition rate as $t \to \infty$. It is also called Fermi's Golden Rule.

Now go back for the other emission process.

$$P_{k,emm} \simeq \frac{\epsilon_0^2| < k|\mu_z|n > |^2}{\hbar^2}\frac{sin^2(\frac{(\omega_{kn}-\omega)t}{2})}{(\omega_{kn} - \omega)^2}$$

As $t \to \infty$

$$\begin{aligned} P_{k,emm} &\simeq \frac{\epsilon_0^2| < k|\mu_z|n > |^2}{\hbar^2}\frac{\pi t}{2}\delta(\omega_{kn} - \omega) \\ &\simeq \frac{\pi\epsilon_0^2| < k|\mu_z|n > |^2}{2\hbar^2}\delta(\omega_{kn} - \omega)t \end{aligned}$$

where $\delta(\omega_{kn} - \omega) = \hbar(\epsilon_{kn} - \epsilon)$. The desired $t \to \infty$ transition probability is therefore

$$\boxed{P_{k,emm} \simeq \tfrac{\pi\epsilon_0^2}{2\hbar}| < k|\mu_z|n > |^2\delta(\epsilon_{kn} - \epsilon)t} \tag{41.16}$$

The transition rate is $R = \frac{dP_{k,emm}}{dt}$ which is

$$\boxed{R_{k,emm} = \tfrac{\pi\epsilon_0^2}{2\hbar}| < k|\mu_z|n > |^2\delta(\epsilon_{kn} - \epsilon)} \tag{41.17}$$

This is the desired transition rate as $t \to \infty$. It is also called Fermi's Golden Rule.

Summary

$$\boxed{P_{k,abs} = \tfrac{\pi}{2\hbar}\epsilon_0^2| < k|\mu_z|n > |^2\delta(\epsilon_{kn} + \epsilon)t} \tag{41.18}$$

$$\boxed{P_{k,emm} \simeq \tfrac{\pi\epsilon_0^2}{2\hbar}| < k|\mu_z|n > |^2\delta(\epsilon_{kn} - \epsilon)t} \tag{41.19}$$

$$\boxed{R_{k,abs} = \tfrac{\pi}{2\hbar}\epsilon_0^2| < k|\mu_z| > n|^2\delta(\epsilon_{kn} + \epsilon)} \tag{41.20}$$

$$\boxed{R_{k,emm} = \tfrac{\pi\epsilon_0^2}{2\hbar}| < k|\mu_z|n > |^2\delta(\epsilon_{kn} - \epsilon)} \tag{41.21}$$

where $t \to \infty$ and in all cases $\epsilon_o = \omega A_o$ and $A_0 = \sqrt{\frac{2\hbar}{\epsilon_0 \omega}(\frac{N}{V})}$. Again recall some texts define $\epsilon_o = -\omega A_o$ due to them using $A = A_o \hat{e} cos(kr - \omega t)$ as opposed to $A = A_o \hat{e} cos(\omega t - kr)$ as done here.

Higher order electric dipole

Finally, one can go to higher orders in the electric dipole approximation by going to more terms in the Taylor series for $e^{ik\cdot r}$ or $e^{-ik\cdot r}$.

$$\begin{aligned} e^{ik\cdot r} &\simeq 1 + ik\cdot r + \ldots \\ e^{-ik\cdot r} &\simeq 1 - ik\cdot r + \ldots \end{aligned}$$

Then $A = A_0 \hat{e} cos(\omega t - k\cdot r)$ becomes

$$\begin{aligned} A &= \frac{A_0 \hat{e}}{2}(e^{i(\omega t - k\cdot r)} + e^{-i(\omega t - k\cdot r)}) \\ &= \frac{A_0 \hat{e}}{2}(e^{i\omega t}e^{-ik\cdot r} + e^{-i\omega t}e^{ik\cdot r}) \end{aligned}$$

where $e^{-ik\cdot r} \simeq 1 - ik\cdot r$ and $e^{ik\cdot r} \simeq 1 + ik\cdot r$

$$\begin{aligned} A &= \frac{A_0 \hat{e}}{2}\left(e^{i\omega t}(1 - ik\cdot r) + e^{-i\omega t}(1 + ik\cdot r)\right) \\ &= \frac{A_0 \hat{e}}{2}\left(e^{i\omega t} - ik\cdot r e^{i\omega t} + e^{-i\omega t} + ik\cdot r e^{-i\omega t}\right) \\ &= \frac{A_0 \hat{e}}{2}\left(e^{i\omega t} + e^{-i\omega t} - ik\cdot r[e^{i\omega t} - e^{-i\omega t}]\right) \end{aligned}$$

$$\boxed{A = A_0 \hat{e}(cos\omega t + k\cdot r sin\omega t)} \tag{41.22}$$

and you can see that $H^{(1)} = -\frac{q}{m}A\cdot P$ becomes much more complicated.

Chapter 42

Second quantization

Now at this point I have 2 choices. I can either related my $R_{k,emm}$ and $R_{k,abs}$ transition rates to what are called Einstein A and B coefficients or I can go and do second quantiztion.

Here is why we will do 2nd quantization first. Einstein's A coefficient represents the rate of spontaneous emission. Recall that I mentioned that one of the problems with a semiclassical treatement of light-matter interacting was that we treated the light classically and matter quantum mechanically when in fact both should have been treated quantum mechanically. As a consequence we found expressions for the transition rate of absorption and stimulated emission but never one for sponetaneous emission.

Hence we will quantize the field here and in turn find that spontaneous emission arises naturally from this treatment and in turn all these derived rates can then be compared to Einstein A and B coefficients.

We found earlier that

$$A = A_0 \hat{e} cos(\omega t - k \cdot r + \phi_p)$$

We can ignore the phase ϕ_P. Also $A_0 = \sqrt{\frac{2\hbar}{\epsilon_0 \omega}(\frac{N}{V})}$. We have

$$A = A_0 \hat{e} cos(\omega t - k \cdot r)$$

We want to express this classical form of the vector potential in a quantum mechanical manner. We will take the vector potential to be a superposition of allowed cavity modes. These cavity modes are subject to boundary conditions and in turn experience quantization effects (i.e. allowed energies or frequencies are restricted)

We will index the cavity modes by k. A will be described as a sum over allowed cavity modes k with a time dependent and spatially dependent component.

$$\boxed{A(r,t) = \sqrt{\tfrac{1}{\epsilon_0 V}}\sum_k q_k(t)\mu_k(r)} \tag{42.1}$$

The sum also runs over 2 possible polarizations for each k but this is suppressed for notational convenience. Here $q_k(t)$ is a time dependent amplitude.

$$\boxed{q_k(t) = |q_k|e^{i\omega_k t}} \tag{42.2}$$

and $\mu_k(r)$ is a position dependent term

$$\boxed{\mu_k(r) = \hat{e}e^{ik\cdot r}} \tag{42.3}$$

An expression for a classical Hamiltonian is given by averaging the energy density over the volume of the cavity. The radiation Hamiltonian is therefore

$$H_{rad} = \int (\text{energy density})dr$$

where the energy density is expressed in SI units.

$$= \frac{(\epsilon_0|E|^2 + \frac{1}{\mu_0}|B|^2)}{2}$$

$$\begin{aligned} H_{rad} &= \int \frac{\epsilon_0|E|^2 + \frac{1}{\mu|B|^2}}{2}dr \\ &= \frac{\epsilon_0}{2}\int |E|^2 + c^2|B|^2 dr \end{aligned}$$

$$\boxed{H_{rad} = \tfrac{\epsilon_0}{2}\int |E|^2 + c^2|B|^2 dr} \tag{42.4}$$

Now we're going to go and solve for this Hamiltonian. Recall that

$$\begin{aligned} E &= -\frac{\partial A}{\partial t} \\ \text{and} & \\ B &= \nabla \times A \end{aligned}$$

From this

$$E = -\sqrt{\frac{1}{\epsilon_0 V}} \sum_k \frac{\partial q_k(t)}{\partial t} \mu_k(r)$$

where $q_k(t) = |q_k| e^{i\omega_k t}$.

Next let's go and find B.

$$B = \nabla \times A = \sqrt{\frac{1}{\epsilon_0 V}} \sum_k q_k(t)(\nabla \times \mu_k(r))$$

where $\mu_k(r) = \hat{e} e^{ik\cdot r}$ and where $\hat{e} = (\hat{x}, \hat{y}, \hat{z})$ Here

$$\nabla \times \mu_k(r) = \begin{vmatrix} i & j & k \\ \frac{\partial}{\partial x} & \frac{\partial}{\partial y} & \frac{\partial}{\partial z} \\ e^{ik\cdot r} & e^{ik\cdot r} & e^{ik\cdot r} \end{vmatrix} \tag{42.5}$$

This reduces to

$$\begin{aligned} = \quad & \hat{i}[\frac{\partial}{\partial y} e^{ik\cdot r} - \frac{\partial}{\partial z} e^{ik\cdot r}], \\ & -\hat{j}[\frac{\partial}{\partial x} e^{ik\cdot r} - \frac{\partial}{\partial z} e^{ik\cdot r}], \\ & \hat{k}[\frac{\partial}{\partial x} e^{ik\cdot r} - \frac{\partial}{\partial y} e^{ik\cdot r}] \end{aligned}$$

$$\begin{aligned} = \quad & \hat{i}[ik_y e^{ik\cdot r} - ik_z e^{ik\cdot r}], \\ & -\hat{j}[ik_x e^{ik\cdot r} - ik_z e^{ik\cdot r}], \\ & \hat{k}[ik_x e^{ik\cdot r} - ik_y e^{ik\cdot r}] \end{aligned}$$

$$= \quad i\left[\hat{i}(k_y e^{ik\cdot r} - k_z e^{ik\cdot r}), -\hat{j}(k_x e^{ik\cdot r} - k_z e^{ik\cdot r}), \hat{k}(k_x e^{ik\cdot r} - k_y e^{ik\cdot r})\right]$$

Claim that this is equivalent to $i(k \times \mu_k)$

Check

$$\begin{vmatrix} \hat{i} & \hat{j} & \hat{k} \\ k_x & k_y & k_z \\ e^{ik\cdot r} & e^{ik\cdot r} & e^{ik\cdot r} \end{vmatrix}$$

This equals

$$\begin{aligned} = \quad & \hat{\imath}(k_y e^{ik\cdot r} - k_z e^{ik\cdot r}), \\ - \quad & \hat{\jmath}(k_x e^{ik\cdot r} - k_z e^{ik\cdot r}), \\ & \hat{k}(k_x e^{ik\cdot r} - k_y e^{ik\cdot r}) \end{aligned}$$

So therefore we see that

$$\nabla \times \mu_k(r) = i(k \times \mu_k(r))$$

Then

$$B = \sqrt{\frac{1}{\epsilon_0 V}} \sum_k i q_k(t)[k \times \mu_k(r)]$$

Consider $\int |E|^2 dr$ and $\int |B|^2 dr$ separately for simplicity and combine them later to get H_{rad}.

$$\begin{aligned} \int |E|^2 dr &= \frac{1}{\epsilon_0 V} \int (\sum_k \frac{\partial q_k^*(t)}{\partial t} \mu_k^*(r))(\sum_k \frac{\partial q_k(t)}{\partial t} \mu_k(r))dr \\ &= \frac{1}{\epsilon_0 V} \sum_k \int \frac{\partial q_k^*(t)}{\partial t} \mu_k^*(r) \frac{\partial_k(t)}{\partial t} \mu_k(r) dr \end{aligned}$$

Remove the time dependent terms

$$= \frac{1}{\epsilon_0 V} \sum_k \frac{\partial_k^*(t)}{\partial t} \frac{\partial q_k(t)}{\partial t} \int \mu_k^*(r) \mu_k(r) dr$$

where $\mu_k^* = \hat{e}e^{-ik\cdot r}$ and $\mu_k = \hat{e}e^{ik\cdot r}$

$$\begin{aligned} &= \frac{1}{\epsilon_0 V} \sum_k \frac{\partial_k^*(t)}{\partial t} \frac{\partial q_k(t)}{\partial t} \int dr \\ &= \frac{1}{\epsilon_0 V} \sum_k \frac{\partial_k^*(t)}{\partial t} \frac{\partial q_k(t)}{\partial t} V \\ &= \frac{1}{\epsilon_0} \sum_k \left| \frac{\partial q_k(t)}{\partial t} \right|^2 \end{aligned}$$

Therefore

$$\boxed{\int |E|^2 dr = \frac{1}{\epsilon_0} \sum_k \left| \frac{\partial q_k(t)}{\partial t} \right|^2} \qquad (42.6)$$

Do the magnetic field term now

$$\begin{aligned}\int |B|^2 dr &= \frac{1}{\epsilon_0 V}\int \sum_k q_k^*(t)[k\times\mu_k(r)]^* \sum_k q_k(t)[k\times\mu_k(r)]dr \\ &= \frac{1}{\epsilon_0 V}\sum_k q_k^*(t)q_k(t)\int [k\times\mu_k(r)]^*[k\times\mu_k(r)]dr \\ &= \frac{1}{\epsilon_0 V}\sum_k |q_k(t)|^2 \int [k\times\mu_k^*(r)][k\times\mu_k(r)]dr\end{aligned}$$

Now invoke a vector math identity

$$\boxed{(A\times B)\cdot(C\times D) = (A\cdot C)(B\cdot D)-(A\cdot D)(B\cdot C)} \tag{42.7}$$

So $[k\times\mu_k^*(r)][k\times\mu_k(r)]$ becomes

$$(k\cdot k)(\mu_k^*(r)\mu_k(r)) - (k\cdot\mu_k^*(r)(\mu_k^*(r)\cdot k)$$

The second term is zero since $\mu_k \propto \hat{e}$ and $\hat{e}\perp k$. Here $\hat{e}$ reflects the polarization and k reflects the direction of travel.

Now $\mu_k^*(r)\mu_k(r) = 1$

$$\begin{aligned} &= \frac{1}{\epsilon_0 V}\sum_k |q_k(t)|^2 \int (k\cdot k)dr \\ &= \frac{1}{\epsilon_0 V}\sum_k k^2|q_k(t)|^2 V \\ &= \frac{1}{\epsilon_0}\sum_k k^2|q_k(t)|^2\end{aligned}$$

therefore

$$\boxed{\int |B|^2 dr = \tfrac{1}{\epsilon_0}\textstyle\sum_k |q_k(t)|^2} \tag{42.8}$$

Now put everything back to evaluate H_{rad}

$$\begin{aligned} H_{rad} &= \frac{\epsilon_0}{2}\int |E|^2 dr + \frac{\epsilon_0 c^2}{2}\int |B|^2 dr \\ &= \frac{\epsilon_0}{2}[\frac{1}{\epsilon_0}\sum_k |\frac{\partial q_k(t)}{\partial t}|^2] + \frac{\epsilon_0 c^2}{2}[\frac{1}{\epsilon_0}\sum_k k^2|q_k(t)|^2] \\ &= \frac{1}{2}\sum_k |\frac{\partial q_k(t)}{\partial t}|^2 + \frac{1}{2}\sum_k k^2c^2|q_k(t)|^2 \\ &= \frac{q}{2}\sum_k [|\frac{\partial q_k(t)}{\partial t}|^2 + k^2c^2|q_k(t)|^2]\end{aligned}$$

Now recall that $\omega_k = kc$

$$= \frac{1}{2}\sum_k \left[|\frac{\partial q_k(t)}{\partial t}|^2 + \omega_k^2 |q_k(t)|^2 \right]$$

Let $P_k(t) = \frac{\partial q_k(t)}{\partial t}$. We then get

$$= \frac{1}{2}\sum_k \left[|P_k(t)|^2 + \omega_k^2 |q_k(t)|^2 \right]$$

Remove $|\ \ |$ as it is understood that P_k and q_k are complex and time dependent.

$$= \frac{1}{2}\sum_k (P_k(t)^2 + \omega_k^2 q_k(t)^2)$$

Finally

$$\boxed{H_{rad} = \frac{1}{2}\sum_k (P_k(t)^2 + \omega_k^2 q_k(t)^2)} \tag{42.9}$$

This is our quantum mechanical Hamiltonian for the radiation field.

Now we will define raising and lowering operators where $a^\dagger$ is a raising or creation operator and a is a lowering or annihilation operator.

$$\boxed{a = \frac{1}{\sqrt{2\hbar\omega_k}}(\omega_k q_k(t) + iP_k(t))} \tag{42.10}$$

$$\boxed{a^\dagger = \frac{1}{\sqrt{2\hbar\omega_k}}(\omega_k q_k(t) - iP_k(t))} \tag{42.11}$$

If you now act on a state with these operators say a state with n number of photons in mode k denoted $|n_k>$ you get

$$\boxed{a^\dagger |n_k> = \sqrt{n_k + 1}|n_k + 1>} \tag{42.12}$$

$$\boxed{a|n_k> = \sqrt{n_k}|n_k - 1>} \tag{42.13}$$

The effect of $a^\dagger$ (raising or creation operator) is to increase the number of photons by 1. Conversely the effect of a (lowering or annihilation operator) is to reduce the number of photons by 1

- $a^\dagger$ is associated with emission
- a is associated with absorption

Now we can re-write H_{rad} in terms of raising and lowering operators just like we did in the harmonic oscillator case.

First evaluate $a^\dagger a$

$$\begin{aligned}
a^\dagger a &= \frac{1}{2\hbar\omega_k}[\omega_k q_k(t) - ip_k(t)][\omega_k q_k(t) + ip_k(t)] \\
&= \frac{1}{2\hbar\omega_k}[\omega_k^2 q_k^2(t) + i\omega_k q_k(t)p_k(t) - i\omega_k p_k(t)q_k(t) + p_k^2(t)] \\
&= \frac{1}{2\hbar\omega_k}[\omega_k^2 q_k^2(t) + p_k^2(t)] + \frac{1}{2\hbar\omega_k}[i\omega_k q_k(t)p_k(t) - i\omega_k p_k(t)q_k(t)] \\
&= \frac{1}{2\hbar\omega_k}[\omega_k^2 q_k^2(t) + p_k^2(t)] + \frac{i}{2\hbar}[q_k(t)p_k(t) - p_k(t)q_k(t)] \\
&= \frac{1}{\hbar\omega_k}[\frac{1}{2}(\omega_k^2 q_k^2(t) + P_k^2(t))] + \frac{i}{2\hbar}[q_k(t), P_k(t)]
\end{aligned}$$

where the last term is a commutator. We get

$$\boxed{a^\dagger a = \frac{H_{rad}}{\hbar\omega_k} + \frac{i}{2\hbar}[q_k(t), P_k(t)]} \tag{42.14}$$

At this point we need to evaluate the commutator explicitly.

First $q_k(t)$

$$\begin{aligned}
a^\dagger &= \frac{1}{\sqrt{2\hbar\omega_k}}(\omega_k q_k(t) - iP_k(t)) \\
a &= \frac{1}{\sqrt{2\hbar\omega_k}}(\omega_k q_k(t) + iP_k(t))
\end{aligned}$$

Put them together

$$\begin{aligned}
(a^\dagger + a) &= \frac{1}{\sqrt{2\hbar\omega_k}}[2\omega_k q_k(t)] \\
&= \sqrt{\frac{2\omega_k}{\hbar}} q_k(t)
\end{aligned}$$

From this

$$\boxed{q_k(t) = \sqrt{\frac{\hbar}{2\omega_k}}(a^\dagger + a)} \tag{42.15}$$

Next for $P_k(t)$

$$\begin{aligned}
a^\dagger &= \frac{1}{\sqrt{2\hbar\omega_k}}(\omega_k q_k(t) - iP_k(t)) \\
a &= \frac{1}{\sqrt{2\hbar\omega_k}}(\omega_k q_k(t) + iP_k(t))
\end{aligned}$$

Putting them together we get

$$\begin{aligned}(a - a^\dagger) &= \frac{1}{\sqrt{2\hbar\omega_k}}(2iP_k(t)) \\ &= \sqrt{\frac{2}{\hbar\omega_k}}iP_k(t)\end{aligned}$$

From this we get

$$\boxed{P_k(t) = i\sqrt{\tfrac{\hbar\omega}{2}}(a^\dagger - a)} \tag{42.16}$$

Now we can go and find the $[q_k(t), P_k(t)]$ commutator. But we need a few more things. We need some common Boson commutation relations.

$$\boxed{[a_k^\dagger, a_k^\dagger] = 0} \tag{42.17}$$

$$\boxed{[a_k, a_k] = 0} \tag{42.18}$$

$$\boxed{[a_k, a_{k'}^\dagger] = \delta_{k,k'}} \tag{42.19}$$

Back to our original commutator

$$\begin{aligned}[q_k(t), P_k(t)] &= q_k(t)P_k(t) - P_k(t)q_k(t) \\ &= \frac{i\hbar}{2}(a^\dagger + a)(a^\dagger - a) - \frac{i\hbar}{2}(a^\dagger - a)(a^\dagger + a) \\ &= \frac{i\hbar}{2}[(a^\dagger a^\dagger - a^\dagger a + aa^\dagger - aa) - (a^\dagger a^\dagger + a^\dagger a - aa^\dagger - aa)] \\ &= \frac{i\hbar}{2}[-a^\dagger a + aa^\dagger - a^\dagger a + aa^\dagger] \\ &= i\hbar[-a^\dagger a + aa^\dagger] \\ &= i\hbar[aa^\dagger - a^\dagger a] \\ &= i\hbar[a, a^\dagger]\end{aligned}$$

where recall that $[a, a^\dagger] = \delta_{k,k'}$ therefore we get

$$\boxed{q_k(t), P_k(t) = i\hbar\delta_{k,k'}} \tag{42.20}$$

Now going back to our expression for $a^\dagger a$

$$\begin{aligned} a^\dagger a &= \frac{H_{rad,k}}{\hbar\omega_k} + \frac{i}{2\hbar}[q_k(t), P_k(t)] \\ &= \frac{H_{rad,k}}{\hbar\omega_k} + \frac{i}{2\hbar}(i\hbar\delta_{k,k'}) \\ &= \frac{H_{rad,k}}{\hbar\omega_k} - \frac{1}{2}\delta_{k,k'} \\ &= \frac{H_{rad,k}}{\hbar\omega_k} - \frac{1}{2} \end{aligned}$$

From this we get

$$\boxed{H_{rad,k} = \hbar\omega_k(a^\dagger a + \tfrac{1}{2})} \tag{42.21}$$

where now $H_{rad} = \sum_k H_{rad,k}$

$$\boxed{H_{rad} = \textstyle\sum_k \hbar\omega_k(a^\dagger a + \tfrac{1}{2})} \tag{42.22}$$

This is our desired form for the radiation Hamiltonian.

Alternatively, let N_k be the number operator and define $N_k = a^\dagger a$. We then get

$$\boxed{H_{rad} = \textstyle\sum_k \hbar\omega_k(N_k + \tfrac{1}{2})} \tag{42.23}$$

Chapter 43

Coupling of radiation to matter

Here we will describe the coupling of radiation to matter using second quantization. We will obtain and expression for the emission transition probability that explicitly includes a term for spontaneous emission.

Recall that $A = A_0 \hat{e} cos(\omega t - k \cdot r + \phi_p)$. We ignore ϕ_p phase so that we get

$$A = A_0 \hat{e} cos(\omega t - k \cdot r)$$

classically and also

$$A = \sqrt{\frac{1}{\epsilon_0 V}} \sum_k q_k(t) \mu_k(t)$$

quantum mechanically where here $q_k(t) = |q| e^{i\omega t}$ and $\mu_k(r) = \hat{e} e^{ik \cdot r}$.

We basically want to express

$$H^{(1)} = -\mu \cdot \epsilon$$

in terms of our new quantized radiation field.

Now like we've always done we will take the electric dipole approximation (or long wavelength approximation) and say $e^{ik \cdot r} \simeq 1$ or $e^{-ik \cdot r} \simeq 1$

$$A = A_0 \hat{e} cos \omega t$$

classically and alternatively

$$A = \sqrt{\frac{1}{\epsilon_0 V}} \sum_k q_k(t) \hat{e}$$

quantum mechanically.

Next we recall from our work on Maxwell's equations that

$$\begin{aligned}\epsilon &= -\frac{\partial A}{\partial t} \\ &= -\sqrt{\frac{1}{\epsilon_0 V}}\sum_k \hat{e}\frac{\partial q_k(t)}{\partial t}\end{aligned}$$

Next recall that we previously defined an operator

$$P_k(t) = \frac{dq_k(t)}{dt}$$

resulting in

$$\epsilon = -\sqrt{\frac{1}{\epsilon_0 V}}\sum_k \hat{e}P_k(t)$$

Ok, now recall that $P_k(t)$ can be defined in terms of photon lowering and raising operators a and $a^\dagger$.

$$\begin{aligned}a^\dagger &= \frac{1}{\sqrt{2\hbar\omega_k}}(\omega_k q_k(t) - iP_k(t)) \\ a &= \frac{1}{\sqrt{2\hbar\omega_k}}(\omega_k q_k(t) + iP_k(t))\end{aligned}$$

where $q_k(t) = |q|e^{i\omega_k t}$. Putting these together we get

$$\begin{aligned}(a - a^\dagger) &= \frac{1}{\sqrt{2\hbar\omega_k}}(2iP_k(t)) \\ &= \frac{i\sqrt{2}}{\sqrt{\hbar\omega_k}}(P_k(t)) \\ &= i\sqrt{\frac{2}{\hbar\omega_k}}P_k(t)\end{aligned}$$

leading to

$$P_k(t) = -i\sqrt{\frac{\hbar\omega_k}{2}}(a - a^\dagger)$$

$$\boxed{P_k(t) = i\sqrt{\tfrac{\hbar\omega_k}{2}}(a^\dagger - a)} \qquad (43.1)$$

Replace this expression into our ϵ expression above

$$\begin{aligned} \epsilon &= -i\sqrt{\frac{1}{\epsilon_0 V}}\sum_k \hat{e}\sqrt{\frac{\hbar\omega_k}{2}}(a^\dagger - a) \\ &= -i\sqrt{\frac{\hbar}{2\epsilon_0 V}}\sum_k \hat{e}\sqrt{\omega_k}(a^\dagger - a) \end{aligned}$$

$$\boxed{\epsilon = -i\sqrt{\tfrac{\hbar}{2\epsilon_0 V}}\sum_k \hat{e}\sqrt{\omega}(a^\dagger(t) - a(t))} \tag{43.2}$$

where we have explicitly shown the time dependences of $a^\dagger$ and a.

Now we know that since $a^\dagger$ and a are linear combinations of $q_k(t)$ and $P_k(t)$ the time dependent term looks like $e^{i\omega_k t}$. But this can be shown explicitly.

$$\begin{aligned} a^\dagger(t) &\rightarrow a^\dagger e^{i\omega_k t} \\ a(t) &\rightarrow ae^{-i\omega_k t}e^{-i\omega_k t} \end{aligned}$$

If you think about it this revealing of a "hidden" exponential term is analogous to flipping from the interaction representation into the Schrodinger representation.

Starting with the Heisenberg equation of motion

$$\frac{da}{dt} = \frac{i}{\hbar}[H, a]$$

where $H = H_{rad} = \hbar\omega_k(a^\dagger a + \frac{1}{2})$.

$$\begin{aligned} &= \frac{i\hbar\omega_k}{\hbar}[a^\dagger a + \frac{1}{2}, a] \\ &= i\omega_k[(a^\dagger a + \frac{1}{2})a - a(a^\dagger a + \frac{1}{2})] \\ &= i\omega_k[a^\dagger aa + \frac{a}{2} - aa^\dagger a - \frac{a}{2}] \\ &= i\omega_k[a^\dagger aa - aa^\dagger a] \\ &= i\omega_k[a^\dagger, a]a \end{aligned}$$

where recall $[a^\dagger, a] = -\delta_{k,k'}$. So we get

$$= -i\omega\delta_{k,k'}a$$

or

$$\begin{aligned} \frac{da}{dt} &= -i\omega a \\ \frac{da}{a} &= -i\omega dt \\ lna &= -i\omega t + const \end{aligned}$$

$$\boxed{a = a_0 e^{-i\omega t}} \tag{43.3}$$

Take the complex conjugate to get

$$\boxed{a^\dagger = a_0^\dagger e^{i\omega t}} \tag{43.4}$$

Now replace this into our expression for ϵ

$$\boxed{\epsilon = -i\sqrt{\frac{\hbar}{2\epsilon_0 V}}\sum_k \hat{e}\sqrt{\omega_k}[a_0^\dagger e^{i\omega_k t} - a_0 e^{-i\omega_k t}]} \tag{43.5}$$

and now replace this into $H^{(1)} = -\mu \cdot \epsilon$

$$\boxed{H^{(1)} = i\sqrt{\frac{\hbar}{2\epsilon_0 V}}\sum_k (\mu \cdot \hat{e}_k)\sqrt{\omega_k}[a_0^\dagger e^{i\omega_k t} - a_0 e^{-i\omega_k t}]} \tag{43.6}$$

Now recall that $a^\dagger$ (creation operator) is related to emission. Conversely a (annihilation operator) is related to absorption. You can do this whole rotating wave typoe of approximation by considering one term or the other (but not both simultaneously).

Now we need to evaluate the transition probability from an initial state n to a final state k.

$$C_k = < k|H^{(1)}|n >$$

Since now both radiation and matter are treated quantum mechanically, we write the total wavefunction as a product of radiation and matter states.

$$\begin{aligned} |n > &\rightarrow |n_1, n_2, n_3, \cdots > |n > \\ |k > &\rightarrow |k_1, k_2, k_3, \cdots > |\kappa > \end{aligned}$$

Therefore we have

$$\boxed{c_\kappa = < \kappa| < k_1, k_2, k_3, \ldots |H^{(1)}|n_1, n_2, n_3, \cdots > |n >} \tag{43.7}$$

Ok, so to simplify life, let's take this rotating wave type of approximation and consider only the absorption part.

$$H^{(1)} = -i\sqrt{\frac{\hbar}{2\epsilon_0 V}}\sum_k (\mu \cdot \hat{e}_k)\sqrt{\omega_k} a_0 e^{-i\omega_k t}$$

then

$$\begin{aligned} C_\kappa &= <\kappa| <k_1, k_2, k_3, \dots| -i\sqrt{\frac{\hbar}{2\epsilon_0 V}}\sum_k (\mu \cdot \hat{e}_k)\sqrt{\omega_k} a_0 e^{-i\omega_k t}|n_1, n_2, n_3, \cdots > |n> \\ &= -i\sqrt{\frac{\hbar}{2\epsilon_0 V}}\sum_k \sqrt{\omega_k} <\kappa| <k_1, k_2, k_3, \dots|(\mu \cdot \hat{e}_k) a_0 e^{-i\omega_k t}|n_1, n_2, n_3, \cdots > |n> \\ &= -i\sqrt{\frac{\hbar}{2\epsilon_0 V}}\sum_k \sqrt{\omega_k} e^{-i\omega_k t} <\kappa| <k_1, k_2, k_3, \dots|(\mu \cdot \hat{e}_k) a_0|n_1, n_2, n_3, \cdots > |n> \\ &= -i\sqrt{\frac{\hbar}{2\epsilon_0 V}}\sum_k \sqrt{\omega_k} e^{-i\omega_k t} <\kappa|(\mu \cdot \hat{e}_k)|n><k_1, k_2, k_3, \dots|a_0|n_1, n_2, n_3, \cdots > \end{aligned}$$

If we take the z component like usual we get $<\kappa|\mu_z|n>$

$$= -i\sqrt{\frac{\hbar}{2\epsilon_0 V}}\sum_k \sqrt{\omega_k} e^{-i\omega_k t} <\kappa|\mu_z|n><k_1, k_2, k_3, \dots|a_0|n_1, n_2, n_3, \cdots >$$

Here recall that $a|n>=\sqrt{n}|n-1>$ (lowering operator)

$$= -i\sqrt{\frac{\hbar}{2\epsilon_0 V}}\sum_k \sqrt{\omega_k}\sqrt{n_k} e^{-i\omega_{kn} t} <\kappa|\mu_{z_k}|n> (\delta_{k1,n1}\delta_{k2,n2}\delta_{k3,n3}\dots)$$

The delta functions just equal 1. We took away a photon from a given mode. The mode stays the same.

$$= -i\sqrt{\frac{\hbar}{2\epsilon_0 V}}\sum_k \sqrt{\omega_k}\sqrt{n_k} e^{-i\omega_{kn} t} <\kappa|\mu_z|n>$$

therefore

$$\boxed{C_k(t) = -i\sqrt{\tfrac{\hbar}{2\epsilon_0 V}}\textstyle\sum_k \sqrt{\omega_k}\sqrt{n_k} e^{-i\omega_{kn} t} <\kappa|\mu_{z_k}|n>} \tag{43.8}$$

Now the transition probabiity is $P_k = |C_k(t)|^2$. We get using the above expression

$$\boxed{P_k(t) = \tfrac{\hbar}{2\epsilon_0 V}\textstyle\sum_k \omega_k n_k| <\kappa|\mu_{z_k}|n> |^2} \tag{43.9}$$

This is the desired form of the absorption transition probability.

Now we focus on the emission.

$$H^{(1)} = i\sqrt{\frac{\hbar}{2\epsilon_0 V}}\sum_k (\mu \cdot \hat{e}_k)\sqrt{\omega_k}a_0^\dagger e^{i\omega_k t}$$

$$\begin{aligned}
C_k(t) &= \; < \kappa| < k_1, k_2, k_3, \dots |i\sqrt{\frac{\hbar}{2\epsilon_0 V}}\sum_k (\mu \cdot \hat{e}_k)\sqrt{\omega_k}a_0^\dagger e^{i\omega_k t}|n_1, n_2, n_3, \cdots > |n> \\
&= i\sqrt{\frac{\hbar}{2\epsilon_0 V}}\sum_k \sqrt{\omega_k}e^{i\omega_k t} < \kappa| < k_1, k_2, k_3, \dots |(\mu \cdot \hat{e}_k)a_0^\dagger|n_1, n_2, n_3, \cdots > |n> \\
&= i\sqrt{\frac{\hbar}{2\epsilon_0 V}}\sum_k \sqrt{\omega_k}e^{i\omega_k t} < \kappa|\mu \cdot \hat{e}_k|n >< k_1, k_2, k_3, \dots |a_0^\dagger|n_1, n_2, n_3, \cdots >
\end{aligned}$$

where $a^\dagger|n >= \sqrt{n+1}|n+1>$ (raising operator)

$$\begin{aligned}
&= i\sqrt{\frac{\hbar}{2\epsilon_0 V}}\sum_k \sqrt{\omega_k}e^{i\omega_k t} < k|\mu \cdot \hat{e}|n> \sqrt{n_k + 1}(\delta_{k1,n1}\delta_{k2,n2}\delta_{k3,n3}\dots) \\
&= i\sqrt{\frac{\hbar}{2\epsilon_0 V}}\sum_k \sqrt{\omega_k}e^{i\omega_k t} < k|\mu \cdot \hat{e}_k|n> \sqrt{n_k + 1}
\end{aligned}$$

Choose the z component like usual to get our desired time dependent coefficient

$$\boxed{C_k(t) = i\sqrt{\tfrac{\hbar}{2\epsilon_0 V}}\textstyle\sum_k \sqrt{\omega_k}e^{i\omega_k t} < k|\mu_{z_k}|n> \sqrt{n_k + 1}} \tag{43.10}$$

Now for the transition probability $P_k = |C_k(t)|^2$

$$\boxed{P_k(t) = \tfrac{\hbar}{2\epsilon_0 V}\textstyle\sum_k \omega_k(n_k + 1)| < k|\mu_{z_k}|n > |^2} \tag{43.11}$$

This is the desired form of the emission transition probability.

You will note that $P_{k,emm}$ is identical to $P_{k,abs}$ except that it has an extra 1 inside. This extra 1 is responsible for spontaneous emission and shows that there is a non-zero probability of emitting a phton even if $n_k = 0$ (the number of photons in a mode).

So we have therefore fixed our problem of not being able to account for spontaneous emission by quantizing the field.

Chapter 44

Alternative coupling of radiation to matter

Rather than use $H^{(1)} = -\mu \cdot \epsilon$ try

$$H^{(1)} = -\frac{q}{m} A \cdot P$$

where

$$A = \sqrt{\frac{1}{\epsilon_0 V}} \sum_k q_k(t) \mu_k(t)$$

and $q_k(t) = |q| e^{i\omega t}$ and $\mu_k(r) = \hat{e}_k e^{ik \cdot r}$.

First take the long wavelength or electric dipole approximation $e^{ik \cdot r} \simeq 1$

$$\begin{aligned} A &= \sqrt{\frac{1}{\epsilon_0 V}} \sum_k q_k(t) \hat{e}_k \\ H^{(1)} &= -\frac{q}{m} \sqrt{\frac{1}{\epsilon_0 V}} \sum_k q_k(t) \hat{e}_k \cdot P \end{aligned}$$

Next recall from our raising and lowering operators that

$$\begin{aligned} a^\dagger &= \frac{1}{\sqrt{2\hbar\omega}} (\omega q_k(t) - i P_k(t)) \\ a &= \frac{1}{\sqrt{2\hbar\omega}} (\omega q_k(t) + i P_k(t)) \end{aligned}$$

Putting them together we get

$$a^\dagger + a = \frac{1}{\sqrt{2\hbar\omega}} 2\omega q_k(t)$$

from this we get

$$\boxed{q_k(t) = \sqrt{\tfrac{\hbar}{2\omega}}(a^\dagger + a)} \tag{44.1}$$

$$\begin{aligned} H^{(1)} &= -\frac{q}{m}\sqrt{\frac{1}{\epsilon_0 V}}\sum_k \sqrt{\frac{\hbar}{2\omega_k}}(a^\dagger + a)(\hat{e}\cdot P) \\ &= -\frac{q}{m}\sqrt{\frac{\hbar}{2\epsilon_0 V}}\sum_k \frac{1}{\sqrt{\omega_k}}(a^\dagger + a)(\hat{e}\cdot P) \end{aligned}$$

where recall that $a^\dagger$ and a have time dependencies. Write it out explicitly.

$$\boxed{a^\dagger(t) = a_0^\dagger e^{i\omega t}} \tag{44.2}$$

$$\boxed{a(t) = a_0 e^{-i\omega t}} \tag{44.3}$$

Again this is analogous to switching from the interaction to the Schrodinger representation.

$$H^{(1)} = -\frac{q}{m}\sqrt{\frac{\hbar}{2\epsilon_0 V}}\sum_k \frac{1}{\sqrt{\omega_k}}[a_0^\dagger e^{i\omega_k}t + a_0 e^{-i\omega_k t}](\hat{e}\cdot P)$$

Now we evaluate matrix elements of $H^{(1)}$ to get the transition probability from an initial state n to a final state k.

Recall that

$$\begin{aligned} |n> &= |n_1, n_2, n_3, \cdots > |n> \\ |\kappa> &= |n_{1'}, n_{2'}, n_{3'}, \cdots > |\kappa> \end{aligned}$$

$$\begin{aligned} C_k(t) &= -\frac{q}{m}\sqrt{\frac{\hbar}{2\epsilon_0 V}}\sum_k \frac{1}{\sqrt{\omega_k}} \\ & < k| < n_{1'}, n_{2'}, n_{3'}, \ldots |(a_0^\dagger e^{i\omega_k t} + a_0 e^{-i\omega_k t})(\hat{e}\cdot P)|n_1, n_2, n_3, \cdots > |n> \end{aligned}$$

Now just like before we evaluate the transition probability for absorption and emission. We can then compare these expression to our previous ones derived using $H^{(1)} = -\mu\cdot\epsilon$. They should be identical

Absorption

$$\begin{aligned}
C_k(t) &= -\frac{q}{m}\sqrt{\frac{\hbar}{2\epsilon_0 V}}\sum_k \frac{1}{\sqrt{\omega_k}} < k| < n_{1'}, n_{2'}, n_{3'}, \dots |a_0 e^{-i\omega_k t}(\hat{e}\cdot P)|n_1, n_2, n_3, \cdots > |n > \\
&= -\frac{q}{m}\sqrt{\frac{\hbar}{2\epsilon_0 V}}\sum_k \frac{1}{\sqrt{\omega_k}} < \kappa|\hat{e}\cdot P|n >< n_{1'}, n_{2'}, n_{3'}, \dots |a_0 e^{-i\omega_k t}|n_1, n_2, n_3, \cdots > \\
&= -\frac{q}{m}\sqrt{\frac{\hbar}{2\epsilon_0 V}}\sum_k \frac{1}{\sqrt{\omega_k}} e^{-i\omega_k t} < \kappa|\hat{e}\cdot P|n >< n_{1'}, n_{2'}, n_{3'}, \dots |a_0|n_1, n_2, n_3, \cdots >
\end{aligned}$$

where $a|n >= \sqrt{n}|n-1>$

$$= -\frac{q}{m}\sqrt{\frac{\hbar}{2\epsilon_0 V}}\sum_k \frac{1}{\sqrt{\omega_k}} e^{-i\omega_k t} < \kappa|\hat{e}\cdot P|n > (\delta_{1',1}\delta_{2',2}\delta_{3',3}\dots)$$

The delta functions all are 1 because we simply extract a photon. The mode stays the same.

$$= -\frac{q}{m}\sqrt{\frac{\hbar}{2\epsilon_0 V}}\sum_k \sqrt{\frac{n_k}{\omega_k}} e^{-i\omega_k t} < k|\hat{e}\cdot P|n >$$

where recall that $P = \frac{im}{\hbar}[H^{(0)}, r]$.

$$= -\frac{q}{m}\sqrt{\frac{\hbar}{2\epsilon_0 V}}\sum_k \sqrt{\frac{n_k}{\omega_k}} e^{-i\omega_k t}\hat{e}\cdot < k|P|n > (\frac{im}{\hbar}) \tag{44.4}$$

$$\begin{aligned}
&= -\frac{q}{m}\sqrt{\frac{\hbar}{2\epsilon_0 V}}\sum_k \sqrt{\frac{n_k}{\omega_k}} e^{-i\omega_k t}\hat{e}\cdot < k|H^{(0)}r - rH^{(0)}| > (\frac{im}{\hbar}) \\
&= -\frac{q}{m}\sqrt{\frac{\hbar}{2\epsilon_0 V}}\sum_k \sqrt{\frac{n_k}{\omega_k}} e^{-i\omega_k t}\hat{e}\cdot [< k|H^{(0)}r|n > - < k|rH^{(0)}|n >](\frac{im}{\hbar}) \\
&= -\frac{q}{m}\sqrt{\frac{\hbar}{2\epsilon_0 V}}\sum_k \sqrt{\frac{n_k}{\omega_k}} e^{-i\omega_k t}\hat{e}\cdot [(\epsilon_k - \epsilon_n) < k|r|n >](\frac{im}{\hbar}) \\
&= -\frac{q}{m}\sqrt{\frac{\hbar}{2\epsilon_0 V}}\sum_k \sqrt{\frac{n_k}{\omega_k}} e^{-i\omega_k t}(\epsilon_k - \epsilon_n) < k|\hat{e}\cdot r| > (\frac{im}{\hbar}) \\
&= -\frac{}{m}\sqrt{\frac{\hbar}{2\epsilon_0 V}}\sum_k \sqrt{\frac{n_k}{\omega_k}} e^{-i\omega_k t}(\epsilon_k - \epsilon_n) < k|\hat{e}\cdot qr|n > (\frac{im}{\hbar})
\end{aligned}$$

where $\mu = qr$ and choosing the z component gives

$$\begin{aligned} &= -\frac{1}{m}\sqrt{\frac{\hbar}{2\epsilon_0 V}}\sum_k \sqrt{\frac{n_k}{\omega_k}} e^{-i\omega_k t}(\epsilon_k - \epsilon_n) < k|\mu_{z_k}|n > (\frac{im}{\hbar}) \\ &= -i\sqrt{\frac{\hbar}{2\epsilon_0 V}}\sum_k \sqrt{\frac{n_k}{\omega_k}}[\frac{(\epsilon_k - \epsilon_n)}{\hbar}] < k|\mu_z|n > e^{-i\omega_k t} \end{aligned}$$

where $\frac{\epsilon_k - \epsilon_n}{\hbar} = \omega_k$

$$= -i\sqrt{\frac{\hbar}{2\epsilon_0 V}}\sum_k \sqrt{n_k}\sqrt{\omega_k} < k|\mu_z|n > e^{-i\omega_k t}$$

$$\boxed{C_k(t) = -i\sqrt{\frac{\hbar}{2\epsilon_0 V}}\sum_k \sqrt{n_k}\sqrt{\omega_k} < k|\mu_z|n > e^{-i\omega_k t}} \tag{44.5}$$

Now $P_{k,abs} = |C_k(t)|^2$

$$\boxed{P_{k,abs} = \frac{\hbar}{2\epsilon_0 V}\sum_k n_k\omega_k| < k|\mu_z|n > |^2} \tag{44.6}$$

This is the desired form of the absorption probability. It is identical to our previous derivation.

Emission

$$\begin{aligned} C_k(t) &= -\frac{q}{m}\sqrt{\frac{\hbar}{2\epsilon_0 V}}\sum_k \frac{1}{\sqrt{\omega_k}} \\ &\quad < \kappa| < n_{1'}, n_{2'}, n_{3'}, \ldots |a_0^\dagger e^{i\omega_k t}(\hat{e}\cdot P)|n_1, n_2, n_3, \cdots > |n > \\ &= -\frac{q}{m}\sqrt{\frac{\hbar}{2\epsilon_0 V}}\sum_k \frac{1}{\sqrt{\omega_k}} e^{i\omega_k t} < \kappa|\hat{e}\cdot P|n > \\ &\quad < n_{1'}, n_{2'}, n_{3'}, \ldots |a_0^\dagger|n_1, n_2, n_3, \cdots > \end{aligned}$$

where $a^\dagger|n >= \sqrt{n+1}|n+1 >$

$$\begin{aligned} &= -\frac{q}{m}\sqrt{\frac{\hbar}{2\epsilon_0 V}}\sum_k \frac{1}{\sqrt{\omega_k}} e^{i\omega_k t} < \kappa|\hat{e}\cdot P|n > \sqrt{n_k+1}(\delta_{1',1}\delta_{2',2}, \delta_{3',3}\ldots) \\ &= -\frac{q}{m}\sqrt{\frac{\hbar}{2\epsilon_0 V}}\sum_k \frac{1}{\sqrt{\omega_k}} e^{i\omega_k t} < \kappa|\hat{e}\cdot P|n > \sqrt{n_k+1} \end{aligned}$$

Now recall that $P = \frac{im}{\hbar}[H^{(0)}, r]$

$$
\begin{aligned}
&= -\frac{q}{m}\sqrt{\frac{\hbar}{2\epsilon_0 V}}\sum_k \frac{1}{\sqrt{\omega_k}}e^{i\omega_k t}\sqrt{n_k+1}\hat{e}\cdot < \kappa|P|n > \\
&= -\frac{q}{m}\sqrt{\frac{\hbar}{2\epsilon_0 V}}\sum_k \frac{1}{\sqrt{\omega_k}}e^{i\omega_k t}\sqrt{n_k+1}(\frac{im}{\hbar})\hat{e}\cdot < \kappa|[H^{(0)}, r]|n > \\
&= -iq\sqrt{\frac{\hbar}{2\epsilon_0 V}}\sum_k \sqrt{\frac{n_k+1}{\omega_k}}\frac{1}{\hbar}e^{i\omega_k t}\hat{e}\cdot < \kappa|H^{(0)}r - rH^{(0)}|n > \\
&= -iq\sqrt{\frac{\hbar}{2\epsilon_0 V}}\sum_k \sqrt{\frac{n_k+1}{\omega_k}}\frac{1}{\hbar}e^{i\omega_k t}\hat{e}\cdot [< \kappa|H^{(0)}r|n > - < \kappa|rH^{(0)}|n >] \\
&= -iq\sqrt{\frac{\hbar}{2\epsilon_0 V}}\sum_k \sqrt{\frac{n_k+1}{\omega_k}}\frac{1}{\hbar}e^{i\omega_k t}\hat{e}\cdot [(\epsilon_\kappa - \epsilon_n) < \kappa|r|n >] \\
&= -iq\sqrt{\frac{\hbar}{2\epsilon_0 V}}\sum_k \sqrt{\frac{n_k+1}{\omega_k}}\frac{\epsilon_\kappa - \epsilon_n}{\hbar}e^{i\omega_k t}\hat{e}\cdot < \kappa|r|n >
\end{aligned}
$$

where $\omega_k = \frac{\epsilon_\kappa - \epsilon_n}{\hbar}$

$$
\begin{aligned}
&= -iq\sqrt{\frac{\hbar}{2\epsilon_0 V}}\sum_k \sqrt{\frac{n_k+1}{\omega_k}}\omega_k e^{i\omega_k t} < k|\hat{e}\cdot r|n > \\
&= -i\sqrt{\frac{\hbar}{2\epsilon_0 V}}\sum_k \sqrt{\omega_k}\sqrt{n_k+1}e^{i\omega_k t} < k|\hat{e}\cdot qr|n >
\end{aligned}
$$

where $\mu = qr$ and where we take the z component.

$$= -i\sqrt{\frac{\hbar}{2\epsilon_0 V}}\sum_k \sqrt{\omega_k}\sqrt{n_k+1}e^{i\omega_k t} < k|\mu_{z_k}|n >$$

Our desired time dependent coefficient is therefore

$$\boxed{C_k(t) = -i\sqrt{\frac{\hbar}{2\epsilon_0 V}}\sum_k \sqrt{\omega_k}\sqrt{n_k+1}e^{i\omega_k t} < k|\mu_{z_k}|n >} \tag{44.7}$$

Now get $P_k(t) = |C_k(t)|^2$

$$\boxed{P_{k,emm}(t) = \frac{\hbar}{2\epsilon_0 V}\sum_k \omega_k(n_k+1)| < k|\mu_{z_k}|n > |^2} \tag{44.8}$$

This is the desired transition probability for the emission. It is identical to our previous expression and as before note the extra 1 which allows for spontaneous emission to occur.

Chapter 45

Emission

In the last section, the absorption coefficient of materials with different dimensionality were shown to be proportional to the calculated joint density of states. In turn, one could predict that the absorption spectrum of these materials would look like. Here we work out the background behind spontaneous emission, a complementary process to absorption.

Preliminaries: Einstein A and B coefficients

Picture a two level system like that shown in the figure.

Here

- N_1 =population in the ground state or alternatively probability of being in the ground state
- N_2 =population in the excited state, alternatively probability of being in the excited state
- g_1 =degeneracy of ground state
- g_2 =degeneracy of excited state
- ρ =the energy density containing thermal and/or external contributions

Three processes were considered

1. absorption with total rate: $B_{12}\rho N_1$
2. stimulated emission with total rate: $B_{21}\rho N_2$

3. spontaneous emission with total rate: AN_2

Putting everything together one obtains the following rate equations for populating either the ground or excited states

$$\begin{aligned} \frac{dN_1}{dt} &= -B_{12}\rho N_1 + B_{21}\rho N_2 + AN_2 \\ \frac{dN_2}{dt} &= B_{12}\rho N_1 - B_{21}\rho N_2 - AN_2 \end{aligned}$$

In equilibrium, the upward and downward rates are equivalent ($\frac{dN_1}{dt} = \frac{dN_2}{dt} = 0$). So using either of the above expressions

$$B_{12}\rho N_1 - B_{21}\rho N_2 - AN_2 = 0$$

or

$$B_{12}\rho N_1 \text{ (upward)} = B_{21}\rho N_2 + AN_2 \text{ (downward)}$$

solving for ρ gives

$$\begin{aligned} \rho &= \frac{AN_2}{B_{12}N_1 - B_{21}N_2} \\ &= \frac{A}{B_{12}\frac{N_1}{N_2} - B_{21}} \end{aligned}$$

where N_1 and N_2 are Boltzman distributed

$$\begin{aligned} N_1 &= \frac{1}{N}\sum_{i=1}^{g_1} e^{-\frac{\varepsilon_1 - \varepsilon_F}{kT}} = \frac{g_1}{N} e^{-\frac{\varepsilon_1 - \varepsilon_0}{kT}} \\ N_2 &= \frac{1}{N}\sum_{i=1}^{g_2} e^{-\frac{\varepsilon_2 - \varepsilon_F}{kT}} = \frac{g_2}{N} e^{-\frac{\varepsilon_2 - \varepsilon_0}{kT}} \end{aligned}$$

and N is a normalization constant. This leads to

$$\frac{N_1}{N_2} = \frac{g_1}{g_2} e^{-\frac{\varepsilon_1 - \varepsilon_2}{kT}} = \frac{g_1}{g_2} e^{\frac{h\nu}{kT}}$$

where $h\nu = \varepsilon_2 - \varepsilon_1$ is the energy of the photon or transition. Replace this into the above expression for ρ giving

$$\rho(\nu) = \frac{A}{B_{12}\frac{g_1}{g_2} e^{\frac{h\nu}{kT}} - B_{21}} \qquad (45.1)$$

This is the expression for the energy density derived by Einstein. Next he realized that this expression had to be equivalent to the Planck distribution for blackbody radiation. Expressed in terms of wavelength, the Planck distribution is (standard textbook expression)

$$\boxed{\rho_P(\lambda) = \tfrac{8\pi hc}{\lambda^5}\left(\tfrac{1}{e^{\frac{hc}{\lambda kT}}-1}\right)} \tag{45.2}$$

Units: J/(unit volume unit wavelength). This expression is interesting from a historical point of view because when the derivative of this expression is set to zero one obtains the Wein displacement law for blackbody radiation. Likewise the integral of this expression gives what's called the Stefan Boltzman law for blackbody radiation. In a sense, knowing or unknowingly, Planck basically explained everything in one shot. Apparently he nearly suffered a nervous breakdown doing it.

Now back to the main discussion. Expressed in terms of ν rather than λ, the Planck energy density is (derived in the next section)

$$\boxed{\rho_P(\nu) = \tfrac{8\pi h\nu^3}{c^3}\left(\tfrac{1}{e^{\frac{h\nu}{kT}}-1}\right)} \tag{45.3}$$

Units: J/(unit volume unit frequency). Note that in general, in the absence of vacuum, the index of refraction must be taken into account when considering the speed of light.

Interlude: Derivation of Planck energy density

Just like in the density of states section, imagine a sphere of radius k with volume

$$V_k = \frac{4}{3}\pi k^3$$

where the volume of a given mode is $k_x k_y k_z$ (assume periodic boundary conditions, though not necessary, just for convenience) and

$$\begin{aligned} k_x &= \frac{2\pi}{L_x} \\ k_y &= \frac{2\pi}{L_y} \\ k_z &= \frac{2\pi}{L_z} \end{aligned}$$

The number of modes in the given sphere is then (look familiar?)

$$N = \frac{V_k}{k_x k_y k_z} = \frac{\frac{4}{3}\pi k^3}{8\pi^3} L_x L_y L_z$$

For a photon now, multiply this by 2 to account for two possible polarizations

$$\begin{aligned} N^{'} &= 2N = 2\frac{\frac{4}{3}\pi k^3}{8\pi^3} L_x L_y L_z \\ &= \frac{k^3}{3\pi^2} L_x L_y L_z \text{ total number of modes} \end{aligned}$$

Consider the volume density

$$\rho = \frac{N^{'}}{L_x L_y L_z} = \frac{k^3}{3\pi^2} = \frac{k^3}{3\pi^2} \text{ number of modes/unit volume} \tag{45.4}$$

Here is where we diverge a little from the past. To get the frequency density, first let $k = \frac{2\pi}{\lambda}$ where $\lambda = \frac{c}{\nu}$. Therefore

$$k = \frac{2\pi\nu}{c}$$

alternatively $2\pi\nu\frac{n}{c}$ if the index of refraction is different from 1. Then ρ becomes

$$\rho = \frac{k^3}{3\pi^2} = \frac{8\pi}{3}\frac{\nu^3}{c^3}$$

Now like before, to get the frequency density (alternatively called the mode density)

$$\rho^{'} = \frac{d\rho}{d\nu} = \frac{8\pi\nu^2}{c^3} \text{ number per unit volume per unit frequency} \tag{45.5}$$

Planck next showed that the average energy per mode is

$$< \varepsilon >= \frac{h\nu}{e^{\frac{h\nu}{kT}} - 1}$$

Note the Bose Einstein form of the equation (photons are bosons). This leads to the Planck distribution

$$\begin{aligned} \rho_p(\nu) &= \rho^{'} < \varepsilon > \\ &= \frac{8\pi\nu^2}{c^3}\left(\frac{h\nu}{e^{\frac{h\nu}{kT}} - 1}\right) \\ &= \frac{8\pi h\nu^3}{c^3}\left(\frac{1}{e^{\frac{h\nu}{kT}} - 1}\right) \end{aligned}$$

Alternative derivation

Consider the volume of a thin shell in k space. The volume is

$$V = 4\pi k^2 dk$$

where k_x, k_y, k_z all equal $\frac{n\pi}{L_{x,y,z}}$. The number of modes, N is then

$$\begin{aligned} N &= \frac{4\pi k^2 dk}{k_x k_y k_z} \\ &= \frac{4\pi k^2 dk}{\pi^3} L_z L_y L_z \end{aligned}$$

Since there are two polarizations, multiply by 2.

$$N = \frac{8\pi k^2 dk}{\pi^3} L_x L_y L_z$$

Now divide by 8 since each corner of an imaginary cube is shared by 8 other neighboring cubes.

$$N = \frac{k^2}{\pi^2} dk L_x L_y L_z$$

Now get the volume density by dividing by $L_x L_y L_z$ giving

$$\rho = \frac{N'}{L_x L_y L_z} = \frac{k^2 dk}{\pi^2}$$

where $k = \frac{2\pi}{\lambda} = \frac{2\pi\nu}{c}$ such that $k^2 = \frac{4\pi^2\nu^2}{c^2}$ and also $dk = \frac{2\pi}{c} d\nu$. We get

$$\begin{aligned} \rho &= \frac{4\pi\nu^2}{c^3}(2\pi) d\nu \\ &= \frac{8\pi\nu^2}{c^3} d\nu \end{aligned}$$

Now consider the frequency density

$$\rho' d\nu = \rho$$

such that

$$\rho' = \frac{8\pi\nu^2}{c^3}$$

Now back to where we left off. Equate the Einstein and Planck relations

$$\frac{A}{B_{12}\frac{g_1}{g_2}e^{\frac{h\nu}{kT}} - B_{21}} = \frac{8\pi h\nu^3}{c^3}\left(\frac{1}{e^{\frac{h\nu}{kT}} - 1}\right)$$

where note again that if the index is not 1 then replace c with $\frac{c}{n}$. Upon examination of the above equation, to achieve equivalence

$$B_{12}\frac{g_1}{g_2} = B_{21} \tag{45.6}$$

More usually you will see $g_1 = g_2$ such that the expression reduces to $B_{12} = B_{21}$. Furthermore

$$\frac{A}{B_{21}} = \frac{8\pi h\nu^3}{c^3}$$

yielding the standard textbook expression

$$\begin{aligned} A &= \frac{8\pi h\nu^3}{c^3}B_{21} \\ &= \frac{8\pi h\nu^3}{c^3}\frac{g_1}{g_2}B_{12} \end{aligned} \tag{45.7}$$

Again, note that if $g_1 = g_2$ you will commonly see written

$$\boxed{A = \frac{8\pi h\nu^3}{c^3}B_{12}} \tag{45.8}$$

Also if the index is not 1 (not vacuum) then replace c with $\frac{c}{n}$ in the above expressions. The above final expression are what are referred to as the relationship between Einstein A and B coefficients. Remember that A is the one associated with spontaneous emission.

Word of caution

The Planck distribution is often written a number of ways. Different texts will have what on the surface appear to be completely different expressions. These difference actually arises because of differing definitions for the "density" being used by the various authors. Previously we saw two expression for the Planck distribution. The first, in terms of wavelength, has units of: number per unit volume per unit wavelength. The second, in terms of frequency, has units of: number per unit volume per unit frequency. Alternatively sometimes what people mean is the same expression but in units of: number per unit volume per unit energy. This is potentially very confusing. One should look very carefully at what is meant by "density". Here we derive this third form of the Planck distribution with units: number per unit volume per unit energy.

Starting with

$$\rho = \frac{8\pi\nu^3}{3}\left(\frac{n}{c}\right)^3 \tag{45.9}$$

where this expression comes from the previous section where we derived the Planck distribution and where also the index of the medium has been explicitly considered (recall, replace c with $\frac{c}{n}$). Rearrange the expression to

$$\rho = \frac{8\pi n^3\nu^3}{3c^3}\left(\frac{h^3}{h^3}\right) = \frac{8\pi n^3(h\nu)^3}{3c^3h^3} = \frac{8\pi n^3\varepsilon^3}{3c^3h^3}$$

Now as before take the derivative with respect to energy to get the energy density

$$\begin{aligned}\rho^{'} = \frac{d\rho}{d\varepsilon} &= \frac{8\pi n^3(3\varepsilon^2)}{3c^3h^3}\\ &= \frac{8\pi n^3\varepsilon^2}{c^3h^3}\\ &= \frac{8\pi n^3(h\nu)^2}{c^3h^3}\\ &= \frac{8\pi n^3\nu^2}{c^3h}\end{aligned}$$

Some authors will leave it at the second step which is just $\rho^{'} = \frac{8\pi n^3\varepsilon^2}{c^3h^3}$. We will go with

$$\rho^{'} = \frac{8\pi n^3\nu^2}{c^3h} \tag{45.10}$$

Now earlier we had the Planck derived average energy to be

$$<\varepsilon>= \frac{h\nu}{e^{\frac{h\nu}{kT}} - 1}$$

This leads to an expression for the average number of photons which is

$$<p>= \frac{<\varepsilon>}{h\nu} = \frac{1}{e^{\frac{h\nu}{kT}} - 1} \tag{45.11}$$

The resulting Planck photon density is

$$\rho_p = \frac{8\pi n^3\nu^2}{c^3 h}\left(\frac{1}{e^{\frac{hv}{kT}}-1}\right) \text{ number per unit volume per unit energy} \tag{45.12}$$

This then leads to another set of relationships between Einstein A and B coefficients

$$\boxed{B_{12} = B_{21}} \tag{45.13}$$

$$\boxed{A = \frac{8\pi n^3\nu^2}{c^3 h}B_{12} \text{ or } = \frac{8\pi n^3\varepsilon^2}{c^3 h^3}B_{12}} \tag{45.14}$$

The only difference between these relations and the previous ones was how the Planck distribution was defined. Number per unit volume per unit energy (as done here) or number per unit volume per unit frequency (as done previously).

Einstein A and B coefficients revisited

In the last section we derived the relationships between the Einstein coefficients for absorption, stimulated emission and spontaneous emission. In this section, let's rederive the expression is a slightly different manner, but in a way that will be useful a little later on.

Let R_{12} be the unit transition rate from the ground state to the excited state (basically the rate constant)

$$\begin{aligned} R_{12} &= P_{abs}\rho d\varepsilon \\ &\equiv B_{12}\rho \end{aligned}$$

where

- ρ is the number of photons per unit volume per unit energy (note the units!)
- $\rho d\varepsilon$ is the number of photons per unit volume
- P_{abs} is the probability for absorption per unit time
- R_{12} is the absorptions per unit volume per unit time

and where $B_{12} = P_{abs}d\varepsilon$

As before set up the rate equations except now consider explicitly the probability of occupied and unoccupied states in the valence and conduction bands. Let

- f_1 =probability of occupied valence band state
- f_2 =probability of occupied conduction band state
- $1 - f_1$ =probability of unoccupied valence band state
- $1 - f_2$ =probability of unoccupied conduction band state

$1 \rightarrow 2$ **transition (absorption) requires**

- valence band state occupied (f_1)
- conduction band state empty ($1 - f_2$)

resulting in the joint probability being $f_1(1 - f_2)$ such that

$$R_{12,abs} = B_{12}\rho f_1(1 - f_2)$$

$2 \rightarrow 1$ **transition (stimulated emission) requires**

- valence band state empty ($1 - f_1$)
- conduction band state occupied (f_2)

resulting in the joint probability being $f_2(1 - f_1)$ such that

$$R_{21,stim} = B_{21}\rho f_2(1 - f_1)$$

$2 \rightarrow 1$ **transition (spontaneous emission) requires**

- valence band state empty ($1 - f_1$)
- conduction band state occupied (f_2)

resulting in the joint probability being $f_2(1 - f_1)$ such that

$$R_{21,spont} = Af_2(1 - f_1)$$

In all three cases f_1 and f_2 are Fermi Dirac distributions

$$\begin{aligned} f_1 &= \frac{1}{e^{\frac{\varepsilon_1 - \varepsilon_F}{kT}} + 1} \\ f_2 &= \frac{1}{e^{\frac{\varepsilon_2 - \varepsilon_F}{kT}} + 1} \end{aligned}$$

At this point, for simplicity, assume that $g_1 = g_2$. At equilibrium the upward and downward rates equal resulting in

$$\begin{aligned} R_{12,abs} &= R_{21,stim} + R_{21,spont} \\ B_{12}\rho f_1(1-f_2) &= B_{21}\rho f_2(1-f_1) + Af_2(1-f_1) \end{aligned}$$

Rearrange this to solve for ρ

$$\rho[B_{12}f_1(1-f_2) - B_{21}f_2(1-f_1)] = Af_2(1-f_1)$$

which gives

$$\begin{aligned} \rho &= \frac{Af_2(1-f_1)}{B_{12}f_1(1-f_2) - B_{21}f_2(1-f_1)} \\ &= \frac{A}{B_{12}\frac{f_1(1-f_2)}{f_2(1-f_1)} - B_{21}} \end{aligned}$$

Now introduce the explicit expression for f_1 and f_2. To simplify

$$\begin{aligned} \frac{f_1(1-f_2)}{f_2(1-f_1)} &= \frac{\left(\frac{1}{e^{\frac{\varepsilon_1-\varepsilon_F}{kT}}+1}\right)\left(1-\frac{1}{e^{\frac{\varepsilon_2-\varepsilon_F}{kT}}+1}\right)}{\left(\frac{1}{e^{\frac{\varepsilon_2-\varepsilon_F}{kT}}+1}\right)\left(1-\frac{1}{e^{\frac{\varepsilon_1-\varepsilon_F}{kT}}+1}\right)} \\ &= e^{\frac{\varepsilon_2-\varepsilon_1}{kT}} \\ &= e^{\frac{h\nu}{kT}} \end{aligned}$$

Replace this into the main expression for ρ to get

$$\rho = \frac{A}{B_{12}\frac{f_1(1-f_2)}{f_2(1-f_1)} - B_{21}} = \frac{A}{B_{12}e^{\frac{h\nu}{kT}} - B_{21}}$$

But ρ equals the Planck distribution for photon density

$$\rho = \frac{A}{B_{12}e^{\frac{h\nu}{kT}} - B_{21}} = \frac{8\pi n^3\nu^2}{c^3 h}\left(\frac{1}{e^{\frac{h\nu}{kT}} - 1}\right)$$

meaning that for this to be true

$$B_{12} = B_{21}$$

and

$$A = \frac{8\pi n^3\nu^2}{c^3 h}B_{12}$$

which are exactly the same Einstein A and B relations we found before.

Emission spectrum

Here we will calculate the emission spectrum of a 3D material using the Einstein A and B coefficients. Define the (net) unit transition rate from the ground state to the excited state.

$$R_{net} = P_{abs}\rho d\varepsilon \tag{45.15}$$

where as before

- ρ is the number of photons per unit volume per unit energy
- $\rho d\varepsilon$ is the number of photons per unit volume
- P_{abs} is the probability for absorption per unit time
- R_{net} is the absorptions per unit volume per unit time

Now consider the net rate upwards from 1 to 2 including stimulated emission

$$\begin{aligned} R_{12,abs} &= B_{12}\rho f_1(1-f_2) \text{ (transition rate per unit volume)} \\ R_{21,stim} &= B_{21}\rho f_2(1-f_1) \text{ (transition rate per unit volume)} \end{aligned}$$

such that the net upwards rate is

$$\begin{aligned} R_{net} &= R_{12,abs} - R_{21,stim} \text{ (transition rate per unit volume)} \\ &= B_{12}\rho f_1(1-f_2) - B_{21}\rho f_2(1-f_1) \end{aligned}$$

Since we have already shown that $B_{12} = B_{21}$

$$R_{net} = B_{12}\rho[f_1(1-f_2) - f_2(1-f_1)] \tag{45.16}$$

Equating the two expressions for ρ gives

$$\begin{aligned} P_{abs}\rho d\varepsilon &= B_{12}\rho[f_1(1-f_2) - f_2(1-f_1)] \\ P_{abs}d\varepsilon &= B_{12}[f_1(1-f_2) - f_2(1-f_1)] \end{aligned}$$

Here we relate P_{abs} to the absorption coefficient as follows

$$P_{abs} = \frac{c}{n}\alpha$$

How? If P is the absolute probability for an absorption event and $\frac{dP}{dt} \equiv P_{abs}$

$$\begin{aligned} \frac{dP}{dt} &= \frac{dP}{dz}\left(\frac{dz}{dt}\right) \\ P_{abs} &= \alpha\left(\frac{c}{n}\right) \end{aligned}$$

Insert this P_{abs} expression into the above equivalence to get

$$\alpha\left(\frac{c}{n}\right)d\varepsilon = B_{12}[f_1(1-f_2) - f_2(1-f_1)]$$

Rearrange this to solve for B_{12}

$$B_{12} = \alpha\left(\frac{c}{n}\right)\frac{d\varepsilon}{[f_1(1-f_2) - f_2(1-f_1)]}$$

Relate B_{12} to A using our derived Einstein A and B coefficients.

$$\begin{aligned} A &= \frac{8\pi n^3\nu^2}{c^3 h}B_{12} = \frac{8\pi\nu^2}{h}\left(\frac{n}{c}\right)^3\alpha\left(\frac{c}{n}\right)\frac{d\varepsilon}{[f_1(1-f_2) - f_2(1-f_1)]} \\ &= \frac{8\pi\nu^2}{h}\left(\frac{n}{c}\right)^2\alpha\frac{d\varepsilon}{[f_1(1-f_2) - f_2(1-f_1)]} \end{aligned}$$

Now recall that

$$R_{21,spont} = Af_2(1-f_1)$$

such that

$$\begin{aligned} R_{21,spont} &= \alpha\frac{8\pi\nu^2}{h}\left(\frac{n}{c}\right)^2\frac{f_2(1-f_1)d\varepsilon}{[f_1(1-f_2) - f_2(1-f_1)]} \\ &= \alpha\frac{8\pi\nu^2}{h}\left(\frac{n}{c}\right)^2\frac{d\varepsilon}{\frac{f_1(1-f_2)}{f_2(1-f_1)} - 1} \end{aligned}$$

Now for convenience define

$$r_{spont}(\varepsilon)d\varepsilon = R_{21}$$

where $r_{spont}(\varepsilon)$ is the transition rate per unit volume per unit energy. By inspection

$$r_{spont}(\varepsilon) = \alpha\frac{8\pi\nu^2}{h}\left(\frac{n}{c}\right)^2\frac{1}{\frac{f_1(1-f_2)}{f_2(1-f_1)} - 1}$$

and

$$\begin{aligned} f_1 &= \frac{1}{e^{\frac{\varepsilon_1-\varepsilon_F}{kT}} + 1} \\ f_2 &= \frac{1}{e^{\frac{\varepsilon_2-\varepsilon_F}{kT}} + 1} \end{aligned}$$

We've solved the ratio in the denominator before giving

$$\frac{f_1(1-f_2)}{f_2(1-f_1)} = e^{\frac{h\nu}{kT}}$$

Putting everything together

$$r_{spont}(\varepsilon) = \alpha\left(\frac{8\pi\nu^2}{h}\right)\left(\frac{n}{c}\right)^2\left(\frac{1}{e^{\frac{h\nu}{kT}}-1}\right)$$

If $h\nu > kT$ the term in parenthesis $\sim e^{-\frac{h\nu}{kT}}$ and the main expression becomes

$$r_{spont}(\varepsilon) = \alpha\left(\frac{8\pi\nu^2}{h}\right)\left(\frac{n}{c}\right)^2 e^{-\frac{h\nu}{kT}} \tag{45.17}$$

We can stop here or continue to express this as an intensity.

$$I_{3D}(\varepsilon) = \varepsilon\frac{r_{spont}(\varepsilon)}{\alpha_{exc}(\varepsilon)}$$

where $\alpha_{exc}(\varepsilon)$ is the absorption coefficient at the particular excitation position. This value is a constant.

$$\begin{aligned} I_{3D}(\varepsilon) &= (h\nu)\frac{\alpha\left(\frac{8\pi\nu^2}{h}\right)\left(\frac{n}{c}\right)^2 e^{-\frac{h\nu}{kT}}}{\alpha_{exc}(\varepsilon)} \\ &= \frac{\alpha}{\alpha_{exc}}(8\pi\nu^3)\left(\frac{n}{c}\right)^2 e^{-\frac{h\nu}{kT}} \qquad (45.18) \end{aligned}$$

Finally, for a 3D material the absorption coefficient is proportional to the joint density of states

$$\alpha \propto A\sqrt{\varepsilon - \varepsilon_g}$$

where A is a constant. This leads to our final expression for the emission spectrum

$$I_{3D} = \frac{A\sqrt{\varepsilon-\varepsilon_g}}{\alpha_{exc}}(8\pi\nu^3)\left(\frac{n}{c}\right)^2 e^{-\frac{h\nu}{kT}}$$

$$\boxed{I_{3D} = A'\sqrt{\varepsilon-\varepsilon_g}e^{-\frac{h\nu}{kT}}} \tag{45.19}$$

Quantum yields and lifetimes

Here we discuss some complementary aspects to the emission. Imagine populating the excited state of the system and immediately (i.e. instantaneously) turning off the light. Basically this is a pulsed experiment.

The depopulation of the excited state occurs by spontaneous emission since stimulated emission only occurs in the presence of the excitation. The relevant rate equation is

$$\frac{dN_2}{dt} = -AN_2$$

or if $A = k_{rad}$

$$\begin{aligned} \frac{dN_2}{dt} &= k_{rad}N_2 \\ \frac{dN_2}{N_2} &= -k_{rad}dt \\ \ln N_2 &= -k_{rad}t + \text{ (const)} \\ N_2 &= Ce^{-k_{rad}t} \end{aligned}$$

At $t = 0$ $C = N_2(0)$ resulting in

$$N_2(t) = N_2(0)e^{-k_{rad}t} \tag{45.20}$$

The decay will be exponential and $\tau = \frac{1}{k_{rad}}$ is called the lifetime of the excited state.

In general, however, since we don't live in a perfect world, there are other de-excitation pathways. These include energy transfer or non-radiative decay through defect states. So in general the total decay rate out of the excited state is the sum of all rates

$$k_{tot} = k_{rad} + k_1 + k_2 + k_3 + \ldots$$

giving

$$\begin{aligned} \frac{dN_2}{dt} &= -(k_{rad} + k_1 + k_2 + k_3 + \ldots)N_2 \\ &= -\left(k_{rad} + \sum_i^n k_i\right) N_2 \\ &= -k_{tot}N_2 \end{aligned}$$

Only the k_{rad} pathway gives you emission. Therefore, the efficiency of emission is called the quantum yield (QY) and is defined by

$$\boxed{QY = \frac{k_{rad}}{k_{tot}} \text{ or } \frac{\frac{1}{\tau_{rad}}}{\frac{1}{\tau_{tot}}} = \frac{\tau_{tot}}{\tau_{rad}}} \tag{45.21}$$

For most applications, one desires a QY that is as close to unity as possible ($QY = 1$). For example, such applications could involve lasers, light emitting diodes, fluorescent tags and so forth.

Chapter 46

Relation to Einstein Coefficients

Previously we had for a harmonic perturbation (monochromatic)

$$P_k \simeq \frac{E_0^2 |<k|\mu_z|n>|^2}{\hbar^2} \frac{sin^2(\frac{(\omega_{kn}-\omega)t}{2})}{(\omega_{kn}-\omega)^2}$$

where $H^{(1)} = -\mu \cdot \epsilon$ and

$$\epsilon = E_0 \hat{e} cos\omega t$$

or

$$\epsilon = E_0 \hat{e} sin\omega t$$

Recall that it didn't really matter which one we chose.

The average energy density in an electromagnetic field is

$$\bar{U} = \frac{\epsilon_0}{2}(|E|^2 + c^2|B|^2)$$

but we showed that $\epsilon_0 |E|^2 = \epsilon_0 c^2 |B|^2$

$$U = \frac{\epsilon_0}{2}(2|E|^2) = \epsilon_0 |E|^2$$

where $E = E_0 \hat{e} cos\omega t$ or $|E|^2 = E_0^2 \hat{e}^2 cos^2\omega t$ but then again the average value of $cos^2\omega t = \frac{1}{2}$. Therefore $|E|^2 = \frac{1}{2}E_0^2$. We now have

$$U = \epsilon_0 \frac{1}{2} E_0^2 = \frac{\epsilon_0 E_0^2}{2}$$

Solve for E_0^2 to get

$$E_0^2 = \frac{2U}{\epsilon_0}$$

and replace this into the above expression for the transition probability.

$$\boxed{P_k = \tfrac{2U}{\epsilon_0 \hbar^2} | < k|\mu_z|n > |^2 \tfrac{sin^2 \frac{(\omega_{kn}-\omega)t}{2}}{(\omega_{kn}-\omega)^2}} \tag{46.1}$$

Now this expression is for a monochromatic perturbation. Like we have done many times in the past, we want an expression that accounts for a broad spread of frequencies where $\rho(\omega_k)d\omega$ is the energy density (per unit volume) and $\rho(\omega_k)$ is the energy density per unit frequency.

$$P_k = \frac{2\rho(\omega_k)d\omega}{\epsilon_0 \hbar^2} | < k|\mu_z|n > |^2 \frac{sin^2 \frac{(\omega_{kn}-\omega)t}{2}}{(\omega_{kn}-\omega)^2}$$

$$P_{k,group} = \frac{2}{\epsilon_0 \hbar^2} | < k|\mu_z|n > |^2 \int_{-\infty}^{\infty} \rho(\omega_k) \frac{sin^2 \frac{(\omega_{kn}-\omega)t}{2}}{(\omega_{kn}-\omega)^2} d\omega_k$$

As before assume that $\rho(\omega_k)$ is constant or uniform.

$$P_{k,group} = \frac{2\rho(\omega_k)| < k|\mu_z|n > |^2}{\epsilon_0 \hbar^2} \int_{-\infty}^{\infty} \frac{sin^2 \frac{(\omega_{kn}-\omega)t}{2}}{(\omega_{kn}-\omega)^2} d\omega_k$$

We have seen integrals like this before. Recall that

$$\int_{-\infty}^{\infty} \frac{sin^2 ax}{x^2} dx = \pi a$$

So therefore in our case by comparison to this

$$\int_{-\infty}^{\infty} \frac{sin^2 \frac{(\omega_{kn}-\omega)t}{2}}{(\omega_{kn}-\omega)^2} d\omega_k = \frac{\pi t}{2}$$

The transition probability then becomes

$$P_{k,group} = \frac{2\rho(\omega_k)| < k|\mu_z|n > |^2}{\epsilon_0 \hbar^2} \frac{\pi t}{2}$$

$$\boxed{P_{k,group} = \tfrac{\pi \rho(\omega_k)}{\epsilon_0 \hbar^2} | < k|\mu_z|n > |^2 t} \tag{46.2}$$

Now let's go for the transition rate. $R = \frac{dP_{k,group}}{dt}$

$$\boxed{R_k = \tfrac{\pi\rho(\omega_k)}{\epsilon_0\hbar^2}| < k|\mu_z|n > |^2} \tag{46.3}$$

This is the desired rate from Fermi's Golden Rule and applies to both absorption and stimulated emission.

Since we took the z component in $| < k|\mu_z|n > |^2$ we should angle average this term

$$\begin{aligned} \mu_z &= \mu cos\theta \\ \mu_z^2 &= \mu_z^2 cos^2\theta \end{aligned}$$

Angle average this

$$\begin{aligned} &= \mu^2\frac{1}{4\pi}\int_0^{2\pi}\int_0^{\pi} cos^2\theta sin\theta d\theta d\phi \\ &= \mu^2\frac{2\pi}{4\pi}\int_0^{\pi} cos^2\theta sin\theta d\theta \\ &= \mu\frac{1}{2}\int_0^{\pi} cos^2\theta sin\theta d\theta \end{aligned}$$

Let $x = cos\theta$ and then $dx = -sin\theta d\theta$. Also remember to change the limits of integration.

$$\begin{aligned} &= -\mu^2\frac{1}{2}\int_1^{-1} x^2 dx \\ &= \mu^2\frac{1}{2}\int_{-1}^{1} x^2 dx \\ &= \mu^2\frac{1}{2}\frac{x^3}{3}\Big|_{-1}^{1} \\ &= \mu^2\frac{1}{2}(\frac{1}{3}+\frac{1}{3}) \\ &= \frac{1}{2}\frac{2}{3} \\ &= \frac{\mu^2}{3} \end{aligned}$$

Therefore

$$\boxed{< | < k|\mu_z|n > |^2 >= \tfrac{|<k|\mu|n>|^2}{3}} \tag{46.4}$$

Now back to our transition probability

$$\boxed{P_{k,angle-avg} = \frac{\pi\rho(\omega_k)}{3\epsilon_0\hbar^2}| < k|\mu|n > |^2} \tag{46.5}$$

By inspection the Einstein B coefficient is

$$\frac{\pi| < k|\mu|n > |^2}{3\epsilon_0\hbar^2}\rho(\omega_k)$$

Therefore

$$\boxed{B_{12} = \frac{\pi|<k|\mu|n>|^2}{3\epsilon_0\hbar^2} = B_{21}} \tag{46.6}$$

Now the relation between Einstein A and B coefficients will depend on how you defined the Placnk distribution. Recall that different people or texts do it slightly differently at times making things potentially very confusing.

We previously had

$$\boxed{A = \frac{8\pi h\nu^3}{c^3}B_{12}} \tag{46.7}$$

We need to convert this into an expression with angular frequency ω. This expression can be rederived to get an expression with ω

$$\boxed{A = \frac{\hbar\omega^3}{\pi^2c^3}} \tag{46.8}$$

into which we introduce our expression for B.

$$\begin{aligned} A &= \left(\frac{\hbar\omega^3}{\pi^2c^3}\right)\frac{\pi| < k|\mu|n > |^2}{3\epsilon_0\hbar^2} \\ &= \frac{\omega^3| < k|\mu|n > |^2}{3\pi c^3\epsilon_0\hbar} \end{aligned}$$

giving our desired expression for the Einstein A coefficient

$$\boxed{A = \frac{\omega^3|<k|\mu|n>|^2}{3\pi\epsilon_0\hbar c^3}} \tag{46.9}$$

Acknowlegements

I'd like to take the opportunity here to thank Istvan Robel for helping me on the home stretch with this workbook. Typing in all these lecture notes into Tex took some time. Istvan provided some nice respite from this work at the end and possibly also saved me from carpal tunnel syndrome.

This workbook was typeset using PC-Tex Version 4.2.05. It was compiled over the course of 1.5 months between the end of August to the end of September 2004.