

Notes on Quantum Mechanics

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Chapter 1

Addition of Angular Momentum

1.1 The General Problem

How do we add an arbitray J_1 and J_2 ? If we did what are their \hat{J}^2 and \hat{J}_z eigenvalues like? One way to do this would be to construct square matrices of the dimension $2j + 1$. However for this we would first need to know the allowed values of j . This we conjecture to be

$$j_1 \otimes j_2 = (j_1 + j_2) \oplus (j_1 + j_2 - 1) \oplus \dots \oplus (j_1 - j_2) \quad (1.1)$$

For our example, the total number of kets is:

$$|jm, j_1 j_2\rangle$$

where

$$\begin{aligned} j_1 + j_2 &\geq j \leq j_1 - j_2 \\ j &\geq m \leq -j \end{aligned}$$

with the normalization conditions:

$$\begin{aligned} \alpha + \beta &= 0 \\ \alpha^2 + \beta^2 &= 1 \end{aligned}$$

1.1.1 Clebsch-Gordan Coefficients

The completeness of the product kets allows us to write,

$$|jm, j_1 j_2\rangle = \sum_{m_1} \sum_{m_2} \langle j_1 m_1, j_2 m_2 | jm, j_1 j_2 \rangle |j_1 m_1, j_2 m_2\rangle \quad (1.2)$$

Here the coefficients of the expansion are termed "Clebsch-Gordan" coefficients. Here are some of their properties:

- $\langle j_1 m_1, j_2 m_2 | j m \rangle \neq 0$ if and only if $j_1 - j_2 \leq j \leq j_1 + j_2$ or $m_1 + m_2 = m$
- $\in \mathbb{R}$
- $\langle j_1 m_1, j_2 m_2 | j m \rangle > 0$
- $\langle j_1 m_1, j_2 m_2 | j m \rangle = (-1)^{j_1 + j_2 - j} \langle j_1 (-m_1), j_2 (-m_2) | j (-m) \rangle$

1.1.2 Modified Spectroscopic Notation

In absence of spin using s,p,d.. is sufficient to describe angular momentum. However, in the presence of spin we change out notation to:

- Use capital letters S,P,D or L typically to indicate the value of angular momentum
- Append a subscript J to the right of L i.e. L_J to indicate the j value
- Append a superscript $2S + 1$ to the left of L i.e. ^{2S+1}L . to indicate the degeneracy due to spin projections

Chapter 2

Approximations

2.1 The Variational Principle

2.1.1 Theorem

Suppose you want to find the ground state energy E_g for a system described by the Hamiltonian H , but you are unable to solve the time-dependent Schrodinger equation. Pick any normalised function ψ whatsoever, then,

$$E_g \leq \langle \psi | H | \psi \rangle \equiv \langle H \rangle \quad (2.1)$$

The expectation value of H in the state ψ is certain to overestimate the ground-state energy. If ψ is an excited state, then it is obvious that the energy is greater than the ground state energy, but the theorem states that the same holds for any ψ whatsoever.

2.1.2 Proof

Since the eigenfunctions of H form a complete set, we can express ψ as a linear combination of them,

$$\psi = \sum_n c_n \psi_n, \text{ with } H\psi_n = E_n \psi_n$$

Since ψ is normalized,

$$1 = \langle \psi | \psi \rangle = \left\langle \sum_m c_m \psi_m \right| \sum_n c_n \psi_n \rangle = \sum_m \sum_n c_m^* c_n \langle \psi_m | \psi_n \rangle = \sum_n |c_n|^2$$

This is under the assumption that the eigenfunctions have been orthonormalized. Meanwhile,

$$\langle H \rangle = \left\langle \sum_m c_m \psi_m \right| H \left| \sum_n c_n \psi_n \right\rangle = \sum_m \sum_n c_m^* E_n c_n \langle \psi_m | \psi_n \rangle = \sum_n E_n |c_n|^2$$

By definition, ground state energy is the smallest eigenvalue, so $E_g \leq E_n$, and hence,

$$\langle H \rangle \geq E_g \sum_n |c_n|^2 = E_g$$

2.1.3 The Ground State of Helium

The helium atom consists of two electrons in orbit around a nucleus containing two protons, and neutrons, but these are irrelevant as we are only considering charge here. The Hamiltonian for this system, ignoring fine structure and smaller corrections is,

$$H = -\frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2) - \frac{e^2}{4\pi\epsilon_0} \left(\frac{2}{r_1} + \frac{2}{r_2} - \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right) \quad (2.2)$$

The ground state energy has been experimentally found out to be,

$$E_g = -78.975 \text{ eV}$$

We are trying to reproduce this value theoretically. This problem has no exact solution due to the electron-electron repulsion,

$$V_{ee} = \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_1 - \mathbf{r}_2|} \quad (2.3)$$

Ignoring this term, H splits into two independent hydrogen Hamiltonians, and the exact solution is just the product of hydrogenic wave functions,

$$\psi_0(\mathbf{r}_1, \mathbf{r}_2) \equiv \psi_{100}(\mathbf{r}_1)\psi_{100}(\mathbf{r}_2) = \frac{8}{\pi a^3} e^{-2(r_1+r_2)/a} \quad (2.4)$$

and the energy is $8E_1 = -109 \text{ eV}$. We can see that this isn't accurate.

To get a better approximation for E_g , we will apply the variational principle using ψ_0 as the trial wave function.

$$H\psi_0 = (8E_1 + V_{ee})\psi_0 \quad (2.5)$$

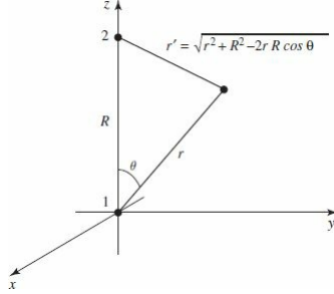
Thus,

$$\langle H \rangle = 8E_1 + \langle V_{ee} \rangle \quad (2.6)$$

Where,

$$\langle V_{ee} \rangle = \left(\frac{e^2}{4\pi\epsilon_0} \right) \left(\frac{8}{\pi a^3} \right)^2 \int \frac{e^{-2(r_1+r_2)/a}}{|\mathbf{r}_1 - \mathbf{r}_2|} d^3\mathbf{r}_1 d^3\mathbf{r}_2 \quad (2.7)$$

The choice of coordinates is as given below,



Integral \mathbf{r}_2 is done first. From law of cosines,

$$|\mathbf{r}_1 - \mathbf{r}_2| = \sqrt{r_1^2 + r_2^2 - 2r_1r_2\cos\theta_2} \quad (2.8)$$

And hence,

$$I_2 \equiv \frac{e^{-4r_2/a}}{|\mathbf{r}_1 - \mathbf{r}_2|} = \int \frac{e^{-4r_2/a}}{\sqrt{r_1^2 + r_2^2 - 2r_1r_2\cos\theta_2}} r_2^2 \sin\theta_2 dr_2 d\theta_2 d\phi_2 \quad (2.9)$$

The ϕ_2 integral equates to 2π , the θ_2 integral is,

$$\begin{aligned} \int_0^\pi \frac{\sin\theta_2}{\sqrt{r_1^2 + r_2^2 - 2r_1r_2\cos\theta_2}} d\theta_2 &= \frac{\sqrt{r_1^2 + r_2^2 - 2r_1r_2\cos\theta_2}}{r_1r_2} \Big|_0^\pi \\ &= \frac{1}{r_1r_2} [(r_1 + r_2) - (r_1 - r_2)] = \begin{cases} 2/r_1, & \text{if } r_2 < r_1 \\ 2/r_2, & \text{if } r_2 > r_1 \end{cases} \end{aligned} \quad (2.10)$$

Thus,

$$\begin{aligned} I_2 &= 4\pi \left(\frac{1}{r_1} \int_0^{r_1} e^{-4r_2/a} r_2^2 dr_2 + \int_{r_1}^\infty e^{-4r_2/a} r_2 dr_2 \right) \\ &= \frac{\pi a^3}{8r_1} \left[1 - \left(1 + \frac{2r_1}{a} e^{-4r_1/a} \right) \right] \end{aligned} \quad (2.11)$$

It then follows that $\langle V_{ee} \rangle$ is equal to,

$$\left(\frac{e^2}{4\pi\epsilon_0} \right) \left(\frac{8}{\pi a^3} \right) \int \frac{\pi a^3}{8r_1} \left[1 - \left(1 + \frac{2r_1}{a} e^{-4r_1/a} \right) \right] e^{-4r_1/a} r_1 \sin\theta_1 dr_1 d\theta_1 d\phi_1$$

The angular integrals are easy (4π) and the r_1 integral becomes,

$$\int_0^\infty \left[r e^{-4r/a} - \left(r + \frac{2r^2}{a} \right) e^{-8r/a} \right] dr = \frac{5a^2}{128}$$

Finally,

$$\langle V_{ee} \rangle = \frac{5}{4a} \left(\frac{e^2}{4\pi\epsilon_0} \right) = -\frac{5}{2}E_1 = 34eV \quad (2.12)$$

And therefore,

$$\langle H \rangle = -109eV + 34eV = -75eV \quad (2.13)$$

This is fairly accurate, but we can improve the result by thinking of a better trial wavefunction. Taking that on average, each electron represents a cloud of negative charge that partially shields the nucleus, so that the other electron sees an effective nuclear charge that is somewhat less than 2.

This suggests that we use a trial function of the form,

$$\psi_1(\mathbf{r}_1\mathbf{r}_2) \equiv \frac{Z^3}{\pi a^3} e^{-Z(r_1+r_2)/a} \quad (2.14)$$

We vary Z as a variational parameter, picking the value that minimizes $\langle H \rangle$. The wavefunction is an eigenstate of the unperturbed hamiltonian, but with Z , instead of 2 in the coulomb terms. We rewrite H ,

$$H = \frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2) - \frac{e^2}{4\pi\epsilon_0} \left(\frac{Z}{r_1} + \frac{Z}{r_2} \right) + \frac{e^2}{4\pi\epsilon_0} \left(\frac{(Z-2)}{r_1} + \frac{(Z-2)}{r_2} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right) \quad (2.15)$$

The expectation value of H is evidently,

$$\langle H \rangle = 2Z^2 E_1 + 2(Z-2) \left(\frac{e^2}{4\pi\epsilon_0} \right) \left\langle \frac{1}{r} \right\rangle + \langle V_{ee} \rangle \quad (2.16)$$

Here the $\langle 1/r \rangle$ is the expectation value of $1/r$ in the hydrogenic ground state ψ_{100} ,

$$\left\langle \frac{1}{r} \right\rangle = \frac{Z}{a} \quad (2.17)$$

Now the expectation value of V_{ee} is,

$$\langle V_{ee} \rangle = \frac{5Z}{8a} \left(\frac{e^2}{4\pi\epsilon_0} \right) = -\frac{5Z}{4}E_1 \quad (2.18)$$

Putting everything together,

$$\langle H \rangle = [2Z^2 - 4Z(Z-2) - (5/4)Z]E_1 = [-2Z^2 + (27/4)Z]E_1 \quad (2.19)$$

According to the variational principle, this quantity exceeds E_g for any value of Z . The lowest upper bound occurs when $\langle H \rangle$ is minimised,

$$\frac{d}{dZ} \langle H \rangle = [-4Z + (27/4)]E_1 = 0 \quad (2.20)$$

from which it follows that,

$$Z = \frac{27}{16} = 1.69 \quad (2.21)$$

This says that the other electron partially screens the nucleus, reducing its effective charge from 2 to 1.69. Substituting this in Z , we find,

$$\langle H \rangle = \frac{1}{2} \left(\frac{3^6}{2} \right) E_1 = -77.5 eV \quad (2.22)$$

Hence we see that the ground state of helium has been calculated with great precision. We can improve this by selecting better trial wavefunctions, but we do not require that since we have already reached within 2% of the correct answer.

2.1.4 The Hydrogen Molecule Ion

Another classic application of the variational principle is to the hydrogen molecule ion, H^+ , consisting of a single electron in the Coulomb field of two protons. Assuming for the moment that the protons are fixed in position, a specified distance R apart, although one of the most interesting byproducts of the calculation is going to be the actual value of R . The Hamiltonian is,

$$H = \frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{r} + \frac{1}{r'} \right) \quad (2.23)$$

Where r and r' are the distances to the electron from the respective protons. Next we try to guess a reasonable trial wavefunction, by taking a hydrogen atom in its ground state,

$$\psi_0(r) = \frac{1}{\sqrt{\pi a^3}} e^{-r/a} \quad (2.24)$$

bringing the second proton in from “infinity,” and nailing it down a distance R away. If R is substantially greater than the Bohr radius, the electron’s wave function probably isn’t changed very much. But we would like to treat the two protons on an equal footing, so that the electron has the

same probability of being associated with either one. This suggests that we consider a trial function of the form,

$$\psi = A[\psi_0(r) + \psi_0(r')] \quad (2.25)$$

Normalising this wave function,

$$1 = \int |\psi|^2 d^3r = |A|^2 \left[\psi_0(r)^2 d^3r + \int \psi_0(r')^2 + 2 \int \psi_0(r)\psi_0(r') d^3r \right] \quad (2.26)$$

Evaluating the integrals give the normalisation factor to be,

$$|A|^2 = \frac{1}{2(1 + I)} \quad (2.27)$$

Where I is,

$$I = e^{-R/a} \left[1 + \frac{R}{a} + \frac{1}{3} \left(\frac{R}{a} \right)^2 \right] \quad (2.28)$$

Now computing the expectation value of the Hamiltonian in the trial state ψ ,

$$\langle H \rangle = \left[1 + 2 \frac{(D + X)}{1 + I} \right] E_1 \quad (2.29)$$

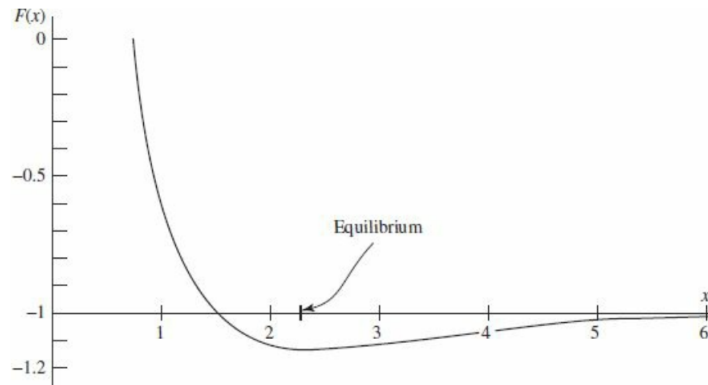
According to the variational principle,

$$V_{pp} = \frac{e^2}{4\pi\epsilon_0} \frac{1}{R} = -\frac{2a}{R} E_1 \quad (2.30)$$

Thus the total energy of the system, in the units of $-E_1$, and expressed as a function of $x \equiv R/\alpha$, is less than,

$$F(x) = -1 + \frac{2}{x} \left\{ \frac{(1 - (2/3)x^2)e^{-x} + (1 + x)e^{-2x}}{1 + (1 + x + (1/3)x^2)e^{-x}} \right\} \quad (2.31)$$

Plotting this function,



Evidently bonding does occur, for there exists a region in which the graph goes below -1 , indicating that the energy is less than that of a neutral atom plus a free proton.

2.2 The WKB Approximation

2.2.1 Introduction

The WKB (Wentzel, Kramers, Brillouin)¹ method is a technique for obtaining approximate solutions to the time-independent Schrödinger equation in one dimension (the same basic idea can be applied to many other differential equations, and to the radial part of the Schrödinger equation in three dimensions). It is particularly useful in calculating bound state energies and tunneling rates through potential barriers. Imagine a particle of energy E moving through a region where the potential $V(x)$ is a constant. if $E > V$, the wavefunction is of the form,

$$\psi(x) = Ae^{\pm ikx}, \text{ with } k \equiv \sqrt{2m(E - V)/\hbar}$$

The plus sign indicates that the particle is traveling to the right, and the minus sign means it is going to the left (the general solution, of course, is a linear combination of the two). The wave function is oscillatory, with fixed wavelength and unchanging amplitude. Now suppose that the potential is not constant, but varies rather slowly in comparison to λ , so that over a region containing many full wavelengths the potential is essentially constant. Then it is reasonable to suppose that ψ remains practically sinusoidal, except that the wavelength and the amplitude change slowly with x . This is the inspiration behind the WKB approximation. In effect, it identifies two different levels of x -dependence: rapid oscillations, modulated by gradual variation in amplitude and wavelength.

If $E < V$,

$$\psi(x) = Ae^{\pm kx}, \text{ with } k \equiv \sqrt{2m(V - E)/\hbar}$$

If $V(x)$ is not constant, but varies slowly in comparison with $1/k$, the solution remains practically exponential. The approximation fails at the classical turning point, where $E \approx V$, where λ goes to infinity.

2.2.2 The Classical Region

The Schrodinger equation,

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + V(x)\psi = E\psi$$

can be rewritten as,

$$\frac{d^2\psi}{dx^2} = -\frac{p^2}{\hbar^2}\psi \tag{2.32}$$

where,

$$p(x) \equiv \sqrt{2m[E - V(x)]} \quad (2.33)$$

is the classical formula for momentum of a particle with total energy E and potential energy $V(x)$. We assume that $E > V$, and this is the classical region and the particle is confined to this range of x . Writing the complex function ψ in terms of amplitude and phase,

$$\psi(x) = A(x)e^{i\phi(x)} \quad (2.34)$$

Using a prime to denote the derivative with respect to x , we find,

$$\frac{d\psi}{dx} = (A' + iA\phi')e^{i\phi}$$

And,

$$\frac{d^2\psi}{dx^2} = [A'' + 2iA'\phi' + iA\phi'' - A(\phi')^2] \quad (2.35)$$

Putting this in equation (32)

$$\frac{d^2\psi}{dx^2} = [A'' + 2iA'\phi' + iA\phi'' - A(\phi')^2] = -\frac{p^2}{\hbar^2}A \quad (2.36)$$

We can split this into two parts, the real and imaginary,

$$A'' - A(\phi')^2 = \frac{-p^2}{\hbar^2}A, \text{ or } A'' = A \left[(\phi')^2 - \frac{p^2}{\hbar^2} \right] \quad (2.37)$$

And,

$$2A'\phi' + A\phi'' = 0, \text{ or } (A^2\phi')' = 0 \quad (2.38)$$

From this we get that,

$$\phi(x) = \pm \frac{1}{\hbar} \int p(x) dx \quad (2.39)$$

And then,

$$\psi(x) \cong \frac{C}{\sqrt{p(x)}} e^{\pm \frac{1}{\hbar} \int p(x) dx} \quad (2.40)$$

And that the general approximate solution will be a linear combination of two of these terms, one with each sign. See that,

$$|\psi(x)|^2 \cong \frac{|C|^2}{p(x)} \quad (2.41)$$

Which says that the probability of finding a particle at point x is inversely proportional to the classical momentum at that point. Sometimes, the WKB approximation is derived from this semiclassical observation.

2.2.3 Tunneling

Now assuming that $E < V$, $p(x)$ becomes imaginary,

$$\psi(x) \cong \frac{C}{\sqrt{|p(x)|}} e^{\pm \frac{1}{\hbar} \int |p(x)| dx} \quad (2.42)$$

Take a problem of scattering from a rectangular barrier with a bumpy top, to the left of the barrier,

$$\psi(x) = Ae^{ikx} + Be^{-ikx} \quad (2.43)$$

To the right of the barrier,

$$\psi(x) = Fe^{ikx} \quad (2.44)$$

Where F is the transmitted amplitude and the tunneling probability is,

$$T = \frac{|F|^2}{|A|^2} \quad (2.45)$$

Our WKB approximation gives us,

$$\psi(x) \cong \frac{C}{\sqrt{|p(x)|}} e^{\pm \frac{1}{\hbar} \int_0^x |p(x')| dx'} + \frac{D}{\sqrt{|p(x)|}} e^{\pm \frac{1}{\hbar} \int_0^x |p(x')| dx'} \quad (2.46)$$

If the barrier is sufficiently wide, the exponentially increasing term diminishes, and the relative amplitudes look like,

$$\frac{|F|}{|A|} \approx e^{\pm \frac{1}{\hbar} \int_0^x |p(x')| dx'}$$

So that,

$$T \cong e^{-2\gamma} \quad (2.47)$$

$$\gamma \equiv \frac{1}{\hbar} \int_0^x |p(x')| dx' \quad (2.48)$$

2.2.4 The connection formulas

We have obtained the wavefunctions for before and after the walls of the potential well, now to determine the region within the potential well, or at a turning point ($E = V$), shifting the axes so that the right hand turning point occurs at $x = 0$, in the WKB approximation we have,

$$\psi(x) \cong \begin{cases} \frac{1}{\sqrt{|p(x)|}} \left[Be^{\frac{1}{\hbar} \int_x^0 |p(x')| dx'} + Ce^{\pm \frac{1}{\hbar} \int_x^0 |p(x')| dx'} \right], & \text{if } x < 0 \\ \frac{1}{\sqrt{|p(x)|}} De^{-\frac{1}{\hbar} \int_0^x |p(x')| dx'} & \text{if } x > 0 \end{cases} \quad (2.49)$$

We essentially patch the two WKB solutions, by using the connection formulas,

$$B = -ie^{i\pi/4}D, \text{ and } C = ie^{-i\pi/4}D \quad (2.50)$$

Now providing the final wavefunction,

$$\psi(x) \cong \begin{cases} \frac{-2D}{\sqrt{|p(x)|}} \sin \left[\frac{1}{\hbar} \int_x^{x_2} |p(x')| dx' + \frac{\pi}{4} \right], & \text{if } x < x_2 \\ \frac{D}{\sqrt{|p(x)|}} e^{-\frac{1}{\hbar} \int_{x_2}^x |p(x')| dx'} & \text{if } x > x_2 \end{cases} \quad (2.51)$$

Where x_2 is an arbitrary point.

2.3 The Adiabatic Approximation

2.3.1 Adiabatic processes

A gradual change in the external conditions characterises an adiabatic process. There are two characteristic times involved, T_i , the internal time, which governs the motion of the system itself and T_e , the external time regarding the change in external parameters.

Suppose that the Hamiltonian changes gradually from some initial form H^i to some final form H^f , the adiabatic theorem states that if the particle was initially in the n th eigenstate of H^i , it will be carried under the Schrodinger equation into the n th eigenstate of H^f .

Take the example of a particle prepared in the ground state of an infinite square well,

$$\psi^i(x) = \sqrt{\frac{2}{a}} \sin \left(\frac{\pi}{a} x \right) \quad (2.52)$$

If we now gradually move the right wall out to $2a$. the adiabatic theorem says that the particle will end up in the ground state of the expanded well,

$$\psi^f(x) = \sqrt{\frac{1}{a}} \sin \left(\frac{\pi}{2a} x \right) \quad (2.53)$$

Note that this change in Hamiltonian isn't small, like perturbation theory, the change can be as huge as needed, but the change should happen slowly is what the adiabatic approximation requires.

2.3.2 Berry's Phase

Now we discuss how the Adiabatic approximation is used in nonholonomic processes, where a system does not return to its original state when transported around a closed loop.

If the Hamiltonian is independent of time, then a particle which starts out in the n th eigenstate $\psi_n(x)$,

$$H\psi_n(x) = E_n\psi_n(x) \quad (2.54)$$

remains in the n^{th} eigenstate, simply picking up a phase factor,

$$\Psi_n(x, t) = \psi_n(x)e^{-iE_nt/\hbar} \quad (2.55)$$

But the adiabatic theorem states that when H changes gradually, the particle remains in the n^{th} eigenstate, even as the eigenfunction itself evolves,

$$\Psi_n(x, t) = \psi_n(x, t)e^{-\frac{i}{\hbar} \int_0^t E_n(t')dt'} e^{i\gamma_n(t)} \quad (2.56)$$

Where the term,

$$\theta_n(t) \equiv -\frac{1}{\hbar} \int_0^t E_n(t')dt' \quad (2.57)$$

Is the dynamic phase and the extra phase, $\gamma_n(t)$ is the geometric phase, which has its significance in the adiabatic theorem.

The net geometric phase change is usually given by,

$$\gamma_n(t) = i \oint \langle \psi_n | \nabla_R \psi_n \rangle \cdot dR \quad (2.58)$$

This is a line integral around a closed loop in parameter space, and its not zero. This is called Berry's phase, and it depends only on the path taken, not on how fast the path is traversed, meanwhile the dynamic phase depends critically on elapsed time

Chapter 3

Perturbation Theory

3.1 Non-Degenerate Perturbation Theory

3.1.1 General Formulation

Suppose we have solved the time-independent Schrodinger wave equation for a given potential (in this case, an infinite potential square well)

$$H^0 \psi_n^0 = E_n^0 \psi_n^0 \quad (3.1)$$

and obtaining a complete set of orthonormal eigenfunctions ψ_n^0 ,

$$\langle \psi_n^0 | \psi_m^0 \rangle = \delta_{nm} \quad (3.2)$$

and the corresponding eigenvalues E_n^0 . If we perturb the potential slightly in the potential well and try to solve for the new eigenvalues and eigenfunctions,

$$H \psi_n = E_n \psi_n \quad (3.3)$$

Here, we use perturbation theory to get approximate solutions to the perturbed problem by building on the exact solutions of the unperturbed case. To begin with, we write the perturbed/new Hamiltonian as the sum of two terms,

$$H = H^0 + \lambda H' \quad (3.4)$$

Where H' is the perturbation. We take λ to be a small number, and the H will be the true, exact Hamiltonian. Writing ψ_n and E_n as a power series in λ , we get,

$$\psi_n = \psi_n^0 + \lambda \psi_n^1 + \lambda^2 \psi_n^2 + \dots \quad (3.5)$$

$$E_n = E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \dots \quad (3.6)$$

Here E_n^1 is the first-order correction to the n^{th} eigenvalue, and ψ_n^1 is the first-order correction to the n^{th} eigenfunction. E_n^2 and ψ_n^2 are the second-order corrections to the eigenvalues and eigenfunctions, and so on. Plugging in Equations (4),(5) and (6) in Equation (3) gives us,

$$(H^0 + \lambda H')[\psi_n^0 + \lambda \psi_n^1 + \lambda^2 \psi_n^2 + \dots] = (E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \dots)[\psi_n^0 + \lambda \psi_n^1 + \lambda^2 \psi_n^2 + \dots] \quad (3.7)$$

We can rewrite Equation (7) by collecting like powers of λ in the form,

$$H^0 \psi_n^0 + \lambda(H^0 \psi_n^1 + H' \psi_n^0) + \lambda^2(H^0 \psi_n^2 + H' \psi_n^1) + \dots \\ E_n^0 \psi_n^0 + \lambda(E_n^0 \psi_n^1 + E_n^1 \psi_n^0) + \lambda^2(E_n^0 \psi_n^2 + E_n^1 \psi_n^1 + E_n^2 \psi_n^0) + \dots$$

We can get the first order (λ^1) equation from Equation (7),

$$H^0 \psi_n^1 + H' \psi_n^0 = E_n^0 \psi_n^1 + E_n^1 \psi_n^0 \quad (3.8)$$

And the second order (λ^2),

$$H^0 \psi_n^2 + H' \psi_n^1 = E_n^0 \psi_n^2 + E_n^1 \psi_n^1 + E_n^2 \psi_n^0 \quad (3.9)$$

And this can be done for higher powers of λ as well.

3.1.2 First order perturbation theory

If we take the inner product of Equation (8), with ψ_n^0 ,

$$\langle \psi_n^0 | H^0 \psi_n^1 \rangle + \langle \psi_n^0 | H' \psi_n^0 \rangle = E_n^0 \langle \psi_n^0 | \psi_n^1 \rangle + E_n^1 \langle \psi_n^0 | \psi_n^0 \rangle \quad (3.10)$$

Because of the useful property of H^0 to be Hermitian, hence Equation (10) becomes,

$$\langle \psi_n^0 | H^0 \psi_n^1 \rangle = \langle H^0 \psi_n^0 | \psi_n^1 \rangle = E_n^0 \langle \psi_n^0 | \psi_n^1 \rangle = \langle E_n^0 \psi_n^0 | \psi_n^1 \rangle \quad (3.11)$$

And hence the terms in Equation (10) cancel out and the property $\langle \psi_n^0 | \psi_n^0 \rangle = 1$ give the equation,

$$E_n^1 = \langle \psi_n^0 | H' | \psi_n^0 \rangle \quad (3.12)$$

This is a fundamental result in first-order perturbation theory, and it states that first-order correction to energy is the expectation value of the perturbation in the unperturbed state.

Now to get the first-order correction to the wave function, we rewrite Equation (8),

$$(H^0 - E_n^0) \psi_n^1 = -(H' E_n^1) \psi_n^0 \quad (3.13)$$

The right side is a known function, so this amounts to an inhomogeneous differential equation for ψ_n^1 . The unperturbed wave functions constitute a complete set, so ψ_n^1 can be written as a linear combination of them,

$$\psi_n^1 = \sum_{m \neq n} c_m^{(n)} \psi_m^0 \quad (3.14)$$

We know that ψ_m^0 satisfies the unperturbed Schrodinger wave equation, so we have,

$$\sum_{m \neq n} (E_m^0 - E_n^0) c_m^{(n)} \psi_m^0 = -(H' - E_n^1) \psi_n^0 \quad (3.15)$$

Taking the inner product with ψ_l^0 ,

$$\sum_{m \neq n} (E_m^0 - E_n^0) c_m^{(n)} \langle \psi_l^0 | \psi_m^0 \rangle = -\langle \psi_l^0 | H' | \psi_n^0 \rangle + E_n^1 \langle \psi_l^0 | \psi_n^0 \rangle \quad (3.16)$$

If $l = n$, is zero, we then get,

$$(E_m^0 - E_n^0) c_l^{(n)} = -\langle \psi_l^0 | H' | \psi_n^0 \rangle \quad (3.17)$$

Or that,

$$c_n^{(n)} = \frac{\langle \psi_m^0 | H' | \psi_n^0 \rangle}{E_n^0 - E_m^0} \quad (3.18)$$

So,

$$\psi_n^1 = \sum_{m \neq n} \frac{\langle \psi_m^0 | H' | \psi_n^0 \rangle}{E_n^0 - E_m^0} \psi_m^0 \quad (3.19)$$

Note that the perturbed energies are surprisingly accurate, while the wave functions are of poor accuracy.

3.1.3 Second order perturbation theory

We take the inner product of the second-order equation with ψ_n^0 ,

$$\langle \psi_n^0 | H^0 \psi_n^2 \rangle + \langle \psi_n^0 | H' \psi_n^1 \rangle = E_n^0 \langle \psi_n^0 | \psi_n^2 \rangle + E_n^1 \langle \psi_n^0 | \psi_n^1 \rangle + E_n^2 \langle \psi_n^0 | \psi_n^0 \rangle \quad (3.20)$$

We exploit the Hermiticity of H^0 ,

$$\langle \psi_n^0 | H^0 \psi_n^2 \rangle = \langle H^0 \psi_n^2 | \psi_n^0 \rangle = E_n^0 \langle \psi_n^0 | \psi_n^2 \rangle \quad (3.21)$$

So the first term on the left cancels the first term on the right. Hence we get the formula for E_n^2 to be,

$$E_n^2 = \langle \psi_n^0 | H' | \psi_n^1 \rangle - E_n^1 \langle \psi_n^0 | \psi_n^1 \rangle \quad (3.22)$$

But,

$$\langle \psi_n^0 | \psi_n^1 \rangle = \sum_{m \neq n} c_m^{(n)} \langle \psi_n^0 | \psi_m^0 \rangle = 0 \quad (3.23)$$

so,

$$E_n^2 = \langle \psi_n^0 | H' | \psi_n^1 \rangle = \sum_{m \neq n} c_m^{(n)} \langle \psi_n^0 | \psi_m^0 \rangle = \sum_{m \neq n} c_m^{(n)} \frac{\langle \psi_m^0 | H' | \psi_n^0 \rangle \langle \psi_m^0 | H' | \psi_n^0 \rangle}{E_n^0 - E_m^0} \quad (3.24)$$

Therefore,

$$E_n^2 = \sum_{m \neq n} c_m^{(n)} \frac{|\langle \psi_m^0 | H' | \psi_n^0 \rangle|^2}{E_n^0 - E_m^0} \quad (3.25)$$

This is the fundamental result of second order perturbation theory.

3.2 Degenerate Perturbation Theory

3.2.1 Motivation

If two or more distinct states, take ψ_a^0 and ψ_b^0 share the same energy, ordinary perturbation theory fails since Equation (25) blows up. So hence we need to obtain a different way to handle the problem.

3.2.2 Twofold Degeneracy

Suppose,

$$\begin{aligned} H^0 \psi_a^0 &= E^0 \psi_a^0 \\ H^0 \psi_b^0 &= E^0 \psi_b^0 \\ \langle \psi_a^0 | \psi_b^0 \rangle &= 0 \end{aligned}$$

And note that any of linear combinations of these states,

$$\psi^0 = \alpha \psi_a^0 + \beta \psi_b^0 \quad (3.26)$$

is still an eigenstate of H^0 , with the same eigenvalue E^0 ,

$$H^0 \psi^0 = E^0 \psi^0 \quad (3.27)$$

When H is perturbed, it breaks the degeneracy. When we increase λ , the common unperturbed energy E^0 splits into two. When we take away the

perturbation, the upper state reduces to one linear combination of ψ_a^0 and ψ_b^0 , and the lower state reduces to some other linear combination. We need to figure out the good linear combinations.

Now writing the good unperturbed states in general form, keeping α and β adjustable and solving the Schrodinger equation,

$$H\psi = E\psi \quad (3.28)$$

With $H = H^0 + \lambda H'$ and,

$$E = E^0 + \lambda E^1 + \lambda^2 E^2 + \dots \quad (3.29)$$

$$\psi = \psi^0 + \lambda \psi^1 + \lambda^2 \psi^2 + \dots \quad (3.30)$$

Plugging these into Equation (28) and collecting like powers of λ , as before, we find,

$$H^0\psi^0 + \lambda(H\psi^0 + H^0\psi^1) + \dots = E^0\psi^0 + \lambda(E^1\psi^0 + E^0\psi^1) + \dots \quad (3.31)$$

But $H^0\psi^0 = E^0\psi^0$, so the first term cancel; at order λ^1 we have,

$$H\psi^0 + H^0\psi^1 = E^1\psi^0 + E^0\psi^1 \quad (3.32)$$

Taking inner product with ψ_a^0 ,

$$\langle \psi_a^0 | H^0 | \psi^1 \rangle + \langle \psi_a^0 | H' | \psi^0 \rangle = E^0 \langle \psi_a^0 | \psi^1 \rangle + E^1 \langle \psi_a^0 | \psi^0 \rangle \quad (3.33)$$

Because H^0 is Hermitian, the first term on the left cancels the term on the right. Putting this in Equation (26), we get,

$$\alpha \langle \psi_a^0 | H' | \psi_a^0 \rangle = \beta \langle \psi_a^0 | H' | \psi_b^0 \rangle = \alpha E^1 \quad (3.34)$$

Or in a more compact form,

$$\alpha W_{aa} + \beta W_{ab} = \alpha E^1 \quad (3.35)$$

Where,

$$W_{ab} = \langle \psi_a^0 | H' | \psi_b^0 \rangle$$

Similarly, the inner product with ψ_b^0 gives us,

$$\alpha W_{ba} + \beta W_{bb} = \beta E^1 \quad (3.36)$$

Now using Equation (35) and (36),

$$\alpha[W_{ab}W_{ba} - (E^1 - W_{aa})(E^1 - W_{bb})] = 0 \quad (3.37)$$

When $\alpha \neq 0$,

$$(E^1)^2 - E^1(W_{aa} + W_{bb}) + (W_{aa}W_{bb} - W_{ab}W_{ba}) = 0 \quad (3.38)$$

Using the quadratic formula and knowing that $W_{ba} = W_{ab}^*$,

$$E_{\pm}^1 = \frac{1}{2} \left[W_{aa} + W_{bb} \pm \sqrt{(W_{aa} - W_{bb})^2 + 4|W_{ab}|^2} \right] \quad (3.39)$$

This is the fundamental result of degenerate perturbation theory, the two roots correspond to the two perturbed energies.

Note that when $\alpha = 0$, we get the nondegenerate perturbation theory (since $\beta = 1$).

3.2.3 Higher-Order Degeneracy

We start by rewriting Equations (35) and (36) in matrix form,

$$\begin{pmatrix} W_{aa} & W_{ab} \\ W_{ba} & W_{bb} \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = E^1 \begin{pmatrix} \alpha \\ \beta \end{pmatrix} \quad (3.40)$$

The E^1 s are the eigenvalues of the W -matrix, Equation (38) being the characteristic equation for this matrix and the good linear combinations of the unperturbed states are the eigenvectors of W . For n -fold degeneracy, we look for the eigenvalues of the $n \times n$ matrix,

$$W_{ij} = \langle \psi_i^0 | H' | \psi_j^0 \rangle \quad (3.41)$$

3.2.4 Lamb Shift

An interesting feature of the fine structure formula is that it depends only on j and not l , moreover in general two different values of l share the same energy. For example, the $2S_{1/2}()$ and $2P_{1/2}()$ states should remain perfectly degenerate. However in 1947 Lamb and Retherford performed an experiment that displayed something to the contrary. The S state is slightly higher in energy than the p state. The explanation of this "Lamb" shift was later explained by Bethe, Feynman, Schwinger and Tomonaga (the founders of QED) as a corollary of the electromagnetic field itself being quantised. Sharply in contrast to the hyperfine structure of Hydrogen, the Lamb shift is a completely novel i.e. non-classical (as the hyperfine structure is explained through Coulomb's law and the Biot-Savart Law) phenomena. It arises from a radiative correction in Quantum Electrodynamics to which classical theories are mute. In Feynman lingo, this arises from loop corrections as portrayed below. Naively,

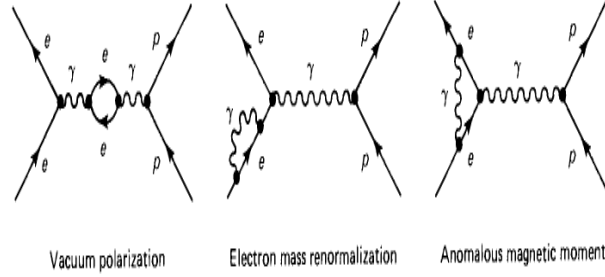


Figure 3.1: Different kinds of radiative corrections

1. the first diagram describes pair-production in the neighborhood of a nucleus, leading to a partial screening effect of the proton's charge;
2. the second diagram reflects the fact that the electromagnetic field has a non-zero ground state
3. the third diagram leads to a tiny modification of the electron's magnetic dipole moment (an addition of $a + \alpha/2\pi = 1.00116$)

We shall not discuss the results in depth but rather consider two exemplary cases:

For $l = 0$,

$$\Delta E_{Lamb} = \alpha^5 mc^2 \frac{1}{4n^3} [k(n, 0)] \quad (3.42)$$

Where $k(n, 0)$ is a numerical factor defined as:

$$k(n, 0) = \begin{cases} 12.7, & \text{if } n = 1 \\ 13.2, & \text{if } n \rightarrow \infty \end{cases}$$

For $l = 0$ and $j = l \pm \frac{1}{2}$,

$$\Delta E_{Lamb} = \alpha^5 mc^2 \frac{1}{4n^3} \left[k(n, 0) \pm \frac{1}{\pi(l + \frac{1}{2})(l + \frac{1}{2})} \right] \quad (3.43)$$

Here, $k(n, l)$ is a very small number (< 0.05) which varies a little with its arguments.

The Lamb shift is tiny except for the case $l = 0$, for which it amounts to about 10% of the fine structure. However, since it depends on l , it lifts the degeneracy of the pairs of states with common n and j and in particular it splits $2S_{1/2}$ and $2P_{1/2}$.

3.3 The Zeeman Effect

When an atom is placed in a uniform magnetic field $B_{Ext.}$, the energy levels are shifted, this is known as the Zeeman effect. For the case of a single electron, the shift is:

$$H'_Z = -(\mu_l + \mu_s).B_{Ext.} \quad (3.44)$$

Where,

$$\mu_s = -\frac{e}{m_e}S \quad (3.45)$$

is the magnetic dipole moment associated with electron spin, and

$$\mu_l = -\frac{e}{2m_e}L \quad (3.46)$$

is the dipole moment associated with orbital motion. The gyromagnetic ratio in this case is simply classical i.e. $q/2m$, it is only for spin that we have an extra factor of 2. We now rewrite (3.44) as:

$$H'_Z = \frac{e}{2m_e}(L + 2S).B_{Ext.} \quad (3.47)$$

The nature of the Zeeman splitting depends on the strength of the external field vs. the internal one that gives rise to spin-orbit/spin-spin coupling. This table provides a short review of the different cases:

Case	Name	Comments
$B_{Ext.} \gg B_{Int.}$	Strong-Field Zeeman Effect	Zeeman effect dominates; fine structure becomes the perturbation
$B_{Ext.} \ll B_{Int.}$	Weak-Field Zeeman Effect	Fine structure dominates; H'_Z can be treated as a small perturbation
$B_{Ext.} = B_{Int.}$	Intermediate Zeeman Effect	Both the fields are equal in strength thus we would need elements of degenerate perturbation theory and will need to diagonalize the necessary portion of the Hamiltonian "by hand"

In the next few sections we'll explore all of them in depth.

3.3.1 Weak-Field Zeeman Effect

Here the fine structure dominates, thus the conserved quantum numbers are n, l, j and m_j , but not m_l and m_s due to the spin-orbit coupling L and S are not separately conserved. Generally speaking, in this problem we have a perturbation pile on top of a perturbation. Thus, the conserved quantum number are those appropriate to the dominant. In first order perturbation theory, the Zeeman correction to energy is,

$$E_Z^1 = \langle nljm_j | H'_Z | nljm_j \rangle = \frac{e}{2m} B_{Ext.} \langle L + 2S \rangle \quad (3.48)$$

Now to figure out $\langle L + 2S \rangle$, we know that $L + 2S = J + S$, this doesn't immediately tell us the expectation value of S but we can figure it out as by understanding that $J = L + S$ is conserved and that the time average of S is simply it's projection along J :

$$S_{Ave} = \frac{(S \cdot J)}{J} J \quad (3.49)$$

But, $L = J - S$, so $L^2 = J^2 + S^2 - 2J \cdot S$, hence:

$$S \cdot J = \frac{1}{2}(J^2 + S^2 - 2J \cdot S) = \frac{\hbar^2}{2}[j(j+1) + s(s+1) - l(l+1)] \quad (3.50)$$

from which it follows that,

$$\langle L + 2S \rangle = \left\langle \left(1 + \frac{S \cdot J}{J^2} J \right) \right\rangle = \left[1 + \frac{j(j+1) - l(l+1) + 3/4}{2j(j+1)} \right] \langle J \rangle \quad (3.51)$$

The term in the square brackets is called the Lande g-factor, denoted by g_j . Now, if we choose B_z to lie along $B_{Ext.}$, then:

$$E_Z^1 = \mu_B g_j B_{Ext.} m_j \quad (3.52)$$

where,

$$\mu_B = \frac{e\hbar}{2m} = 5.788 \times 10^{-5} \text{ eV} T^{-1}$$

is the so called Bohr magneton. The total energy is the sum of the fine-structure part and the Zeeman contribution, in the ground state i.e. $n = 1, l = 0, j = 1/2$ and therefore, $g_J = 2$, it splits into two levels:

$$-13.6 \text{ eV} (1 + \alpha^2/4) \pm \mu_B B_{Ext.} \quad (3.53)$$

with different signs for different m_j 's this is plotted below.

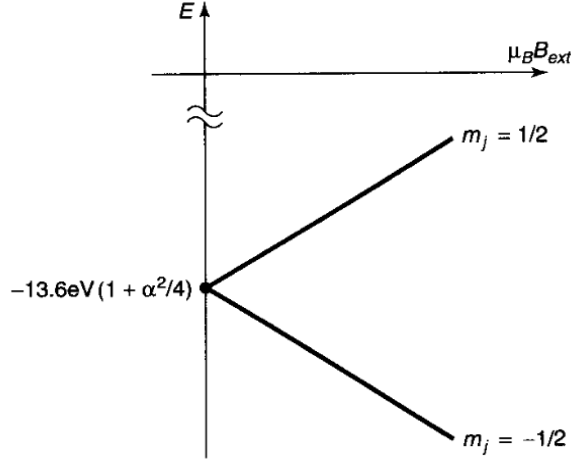


Figure 3.2: Weak-field Zeeman splitting of the ground state of hydrogen; the upper line has a slope of 1 and the lower line a slope of -1

3.3.2 Strong-Field Zeeman Effect

In this case, the Zeeman effect is often referred to as the "Paschen-Back" effect. The conserved quantum numbers are now but and because in the presence of an external torque, the total angular momentum is not conserved but the it's individual components are. The Zeeman Hamiltonian is,

$$H'_Z = \frac{e}{2m} B_{Ext.} (L_z + 2S_z) \quad (3.54)$$

and the unperturbed energies are:

$$E_{nm_l m_s} = -\frac{13.6 \text{ eV}}{n^2} + \mu_B B_{Ext.} (m_l + 2m_s) \quad (3.55)$$

This would be our result if we ignore the fine structure completely. However, we need to take that into account as well. In first-order perturbation theory, the fine structure correction to these levels is:

$$E_{fs}^1 = \langle n \ l \ m_l \ m_s | H'_r + H'_{so} | n \ l \ m_l \ m_s \rangle \quad (3.56)$$

The relativistic contribution is the same as before for the spin-orbit term, we need

$$\langle S.L \rangle = \langle S_x \rangle \langle L_x \rangle + \langle S_y \rangle \langle L_y \rangle + \langle S_z \rangle \langle L_z \rangle = \hbar^2 m_l m_s \quad (3.57)$$

Here $\langle S_x \rangle = \langle S_y \rangle = \langle L_x \rangle = \langle L_y \rangle = 0$ for the eigenstates of S_z and L_z . Putting it all together:

$$E_{fs}^1 = \frac{13.6 \text{ eV}}{n^3} \alpha^2 \left(\frac{3}{4n} - \left[\frac{l(l+1) - m_l m_s}{l(l+1/2)(l+1)} \right] \right) \quad (3.58)$$

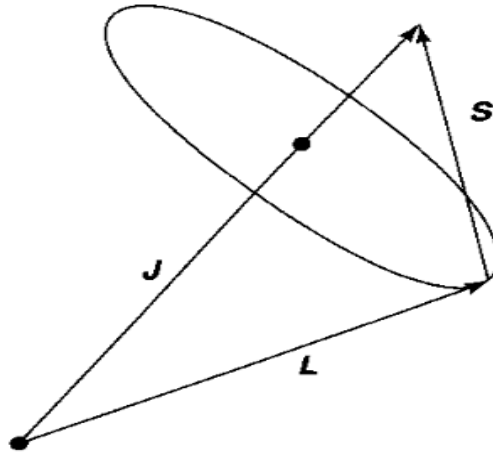


Figure 3.3: In the presence of spin-orbit coupling, L and S are not separately conserved, they precess about the fixed total angular momentum J

The term in the square brackets is indeterminate for $l = 0$, its correct value in this case is 1. The total energy here is the sum of the Zeeman part and the fine structure contribution.

3.3.3 Intermediate Zeeman Effect

In this case, we must treat both the effects as perturbations to the Bohr Hamiltonian,

$$H' = H'_Z + H'_{fs} \quad (3.59)$$

In section we'll discuss the case $n = 2$, and use it as the basis for degenerate perturbation theory. The states here are characterized by l , j and m_j . We could use l, m_l, m_s states but this makes the matrix elements of H'_Z easier to deal with but that of H'_{fs} difficult. Using the Clebsch-Gordan coefficients to express $|jm_j\rangle$ as a linear combination of $|lm_l\rangle |sm_s\rangle$ we have:

$$l = 0 = \begin{cases} \psi_1 & |\frac{1}{2} \frac{1}{2}\rangle = |0 \ 0\rangle |\frac{1}{2} \frac{1}{2}\rangle \\ \psi_2 & |\frac{1}{2} \frac{-1}{2}\rangle = |0 \ 0\rangle |\frac{1}{2} \frac{-1}{2}\rangle \end{cases}$$

$$l = 1 = \begin{cases} \psi_3 & \left| \frac{3}{2} \frac{3}{2} \right\rangle = |1 \ 1\rangle \left| \frac{1}{2} \frac{1}{2} \right\rangle \\ \psi_4 & \left| \frac{3}{2} \frac{-3}{2} \right\rangle = |1 \ -1\rangle \left| \frac{1}{2} \frac{-1}{2} \right\rangle \\ \psi_5 & \left| \frac{3}{2} \frac{1}{2} \right\rangle = \sqrt{2/3} |1 \ 0\rangle \left| \frac{1}{2} \frac{1}{2} \right\rangle + \sqrt{1/3} |1 \ 1\rangle \left| \frac{1}{2} \frac{-1}{2} \right\rangle \\ \psi_6 & \left| \frac{1}{2} \frac{1}{2} \right\rangle = -\sqrt{1/3} |1 \ 0\rangle \left| \frac{1}{2} \frac{1}{2} \right\rangle + \sqrt{2/3} |1 \ 1\rangle \left| \frac{1}{2} \frac{-1}{2} \right\rangle \\ \psi_7 & \left| \frac{3}{2} \frac{-1}{2} \right\rangle = \sqrt{1/3} |1 \ -1\rangle \left| \frac{1}{2} \frac{1}{2} \right\rangle + \sqrt{2/3} |1 \ 0\rangle \left| \frac{1}{2} \frac{-1}{2} \right\rangle \\ \psi_8 & \left| \frac{1}{2} \frac{-1}{2} \right\rangle = -\sqrt{2/3} |1 \ -1\rangle \left| \frac{1}{2} \frac{1}{2} \right\rangle + \sqrt{1/3} |1 \ 0\rangle \left| \frac{1}{2} \frac{-1}{2} \right\rangle \end{cases}$$

In this basis the matrix the non-zero elements of H'_{fs} are all on the diagonal and are given by the Bohr model. H'_z has four off diagonal elements. The complete matrix, W as we will see is more complicated but its eigenvalues are the same since they are independent of the chosen basis.

$$\begin{pmatrix} 5\gamma - \beta & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 5\gamma + \beta & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \gamma - 2\beta & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \gamma + 2\beta & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \gamma - \frac{2}{3}\beta & \frac{\sqrt{2}}{3}\beta & 0 & 0 \\ 0 & 0 & 0 & 0 & \frac{\sqrt{2}}{3}\beta & 5\gamma - \frac{1}{3}\beta & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \gamma + \frac{2}{3}\beta & \frac{\sqrt{2}}{3}\beta \\ 0 & 0 & 0 & 0 & 0 & 0 & \frac{\sqrt{2}}{3}\beta & 5\gamma + \frac{1}{3}\beta \end{pmatrix} \quad (3.60)$$

Where,

$$\gamma = (\alpha/8)^2 13.6 \text{ eV}$$

and,

$$\beta = \mu_B B_{Ext.}$$

The first four eigenvalues are already displayed along the diagonal. We only need to find the eigenvalues of the two 2×2 blocks. The characteristic equation for the first one is given as:

$$\lambda^2 - \lambda(6\gamma - \beta) + \left(5\gamma^2 - \frac{11}{3}\gamma\beta\right) = 0 \quad (3.61)$$

and the quadratic formula gives the eigenvalues:

$$\lambda_{\pm} = 3\gamma - (\beta/2) \pm \sqrt{4\gamma^2 + (2/3)\gamma\beta + (\beta^2/4)} \quad (3.62)$$

The eigenvalues of the second block are the same but with the sign of β reversed. The eight energy levels are listed in the table and are plotted against in the figure (). In the zero field limit they reduce to the fine structure values. For the other cases, the splitting is seen clearly.

ϵ_1	$=$	$E_2 - 5\gamma + \beta$
ϵ_2	$=$	$E_2 - 5\gamma - \beta$
ϵ_3	$=$	$E_2 - \gamma + 2\beta$
ϵ_4	$=$	$E_2 - \gamma - 2\beta$
ϵ_5	$=$	$E_2 - 3\gamma + \beta/2 + \sqrt{4\gamma^2 + (2/3)\gamma\beta + \beta^2/4}$
ϵ_6	$=$	$E_2 - 3\gamma + \beta/2 - \sqrt{4\gamma^2 + (2/3)\gamma\beta + \beta^2/4}$
ϵ_7	$=$	$E_2 - 3\gamma - \beta/2 + \sqrt{4\gamma^2 - (2/3)\gamma\beta + \beta^2/4}$
ϵ_8	$=$	$E_2 - 3\gamma - \beta/2 - \sqrt{4\gamma^2 - (2/3)\gamma\beta + \beta^2/4}$

Figure 3.4: Energy levels for the $n = 2$ states of hydrogen, with fine structure and Zeeman splitting

3.4 Hyperfine Splitting in Hydrogen

The proton also has a magnetic dipole moment, however this is much smaller than that of the electron due to the mass of the proton. It is given by,

$$\mu_p = \frac{g_p e}{2m_p} S_p \quad (3.63)$$

And the magnetic dipole moment of the electron,

$$\mu_e = -\frac{e}{m_e} S_e \quad (3.64)$$

Classically speaking, the dipole μ sets up a magnetic field:

$$B = \frac{\mu_0}{4\pi r^3} [3(\mu \cdot \hat{r})\hat{r} - \mu] + \frac{2\mu_0}{3} \mu \delta^3(r) \quad (3.65)$$

So the Hamiltonian of the electron, in the magnetic field due to the proton's magnetic dipole moment, is

$$H'_{hf} = \frac{\mu_0 g_p e^2}{8\pi m_p m_e} \frac{[3(S_p \cdot \hat{r})(S_e \cdot \hat{r}) - S_p \cdot S_e]}{r^3} + \frac{\mu_0 g_p e^2}{3m_p m_e} S_p \cdot S_e \delta^3(r) \quad (3.66)$$

According to perturbation theory, the first-order correction to the energy is the expectation value of the perturbing Hamiltonian:

$$E_{hf}^1 = \frac{\mu_0 g_p e^2}{8\pi m_p m_e} \left\langle \frac{3(S_p \cdot \hat{r})(S_e \cdot \hat{r}) - S_p \cdot S_e}{r^3} \right\rangle + \frac{\mu_0 g_p e^2}{3m_p m_e} \langle S_p \cdot S_e \rangle |\psi(0)|^2 \quad (3.67)$$

In the ground state or any other state at which $l = 0$, the wavefunction is spherically symmetrical, and the first expectation value vanishes. Meanwhile,

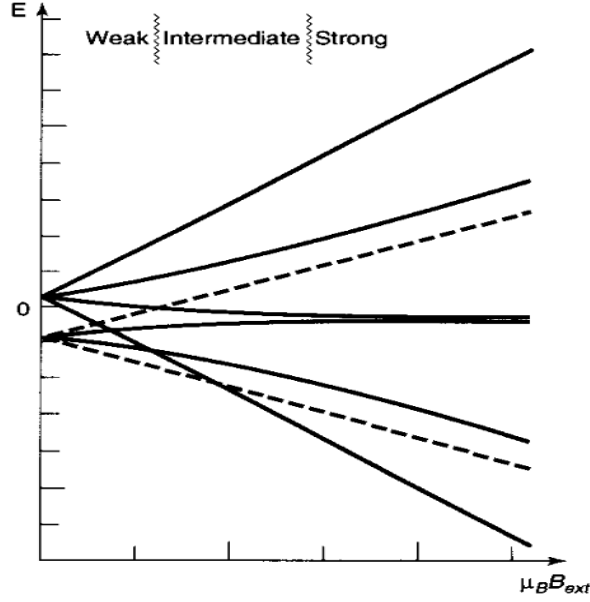


Figure 3.5: Zeeman splitting of the $n = 2$ states of hydrogen, in the weak, intermediate and strong field regimes

from the Schrodinger equation in three dimensions, we find that $|\psi(0)|^2 = 1/(\pi a^3)$, thus,

$$E_{hf}^1 = \frac{\mu_0 g_p e^2}{3\pi m_p m_e a^3} \langle S_p \cdot S_e \rangle \quad (3.68)$$

in the ground state. This is called Spin-Spin coupling because it involves the dot product of two spins in contrast with spin-orbit coupling which involves $S \cdot L$. In the presence of spin-spin coupling, the individual spin angular momenta are no longer conserved. However the eigenvectors of the total spin is conserved:

$$S = S_e + S_p \quad (3.69)$$

We square this out to get,

$$S_p \cdot S_e = \frac{1}{2}(S^2 - S_e^2 - S_p^2) \quad (3.70)$$

But the electron and proton both have spin $1/2$, so $S_e^2 = S_p^2 = (3/4)\hbar^2$. In the triplet i.e. parallel spin state, the total spin is 1, and hence $S^2 = 2\hbar^2$. In the singlet state the total spin is 0, and $S^2 = 0$. Thus,

$$E_{hf}^1 = \frac{4g_p \hbar^4}{3m_p m_e^2 c^2 \alpha^4} \begin{cases} +1/4, & \text{(triplet);} \\ -3/4, & \text{(singlet)} \end{cases} \quad (3.71)$$

The Spin-Spin coupling breaks the spin degeneracy of the ground state, lifting the triplet and depressing the singlet, leading to an energy gap. The energy gap is given by:

$$\Delta E = \frac{4g_p\hbar^4}{3m_pm_e^2c^2\alpha^4} = 5.88 \times 10^{-6} \text{ eV} \quad (3.72)$$

The frequency of the photon emitted when the triplet transitions to a singlet

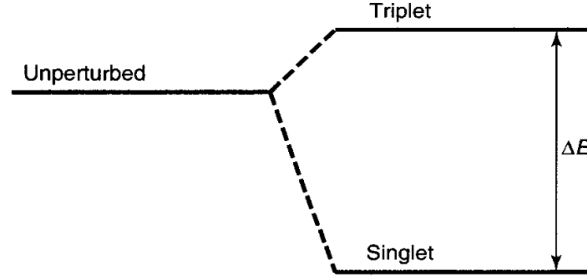


Figure 3.6: Hyperfine splitting in the ground state of Hydrogen

state is:

$$\nu = \frac{\Delta E}{h} = 1420 \text{ MHz} \quad (3.73)$$

The corresponding wavelength is 21 cm which falls in the microwave region. It permeates the universe and is a very important part of Astrophysics.

3.5 Introduction to quantum dynamics

So far, we looked at systems that were time-independent of sorts (quantum statics), and the potentials themselves were time independent, in other words, $V(r, t) = V(r)$. Hence the time-dependent Schrodinger equation took the form,

$$H\psi = i\hbar \frac{\partial \psi}{\partial t} \quad (3.74)$$

And solving by separation of variables,

$$\psi(r, t) = \psi(r)e^{iEt/\hbar} \quad (3.75)$$

where $\psi(r)$ satisfies the time independent Schrodinger equation,

$$H\psi = E\psi \quad (3.76)$$

Due to the nature of the term that carries time dependence, the exponential factor $e^{iEt/\hbar}$, this term cancels out when we construct the physically relevant quantity $|\psi|^2$, which leads to all the expectation values and probabilities to be constant in time, and this is the same case in more complex states where we have linear combinations of these stationary states.

For us, if we want to investigate transitions between one energy level to another, we introduce a time-dependent potential, hence the name of quantum dynamics arises.

3.6 Two level systems

3.6.1 Introduction

Let us suppose that there are two states of the unperturbed system, ψ_a and ψ_b . They are eigenstates of the unperturbed Hamiltonian, H_0 ,

$$H_0\psi_a = E_a\psi_a \text{ and } H_0\psi_b = E_b\psi_b \quad (3.77)$$

and they are orthonormal,

$$\langle\psi_a|\psi_b\rangle = \delta_{ab} \quad (3.78)$$

And any state can be expressed as a linear combination of them, or in particular,

$$\Psi(0) = c_a\psi_a + c_b\psi_b \quad (3.79)$$

In the absence of perturbation, each component evolves with its characteristic exponential factor.

$$\Psi(t) = c_a\psi_a e^{-iE_a t/\hbar} + c_b\psi_b e^{-iE_b t/\hbar} \quad (3.80)$$

Calculating $|c_a|^2$ is the probability that the particle is in the state ψ_a , and the measurement of the energy will yield E_a . Normalizing Ψ ,

$$|c_a|^2 + |c_b|^2 = 1 \quad (3.81)$$

3.6.2 The perturbed system

Turning on a time-dependent perturbation $H'(t)$, the coefficients c_a and c_b become functions of t and the equation then becomes,

$$\Psi(t) = c_a(t)\psi_a e^{-iE_a t/\hbar} + c_b(t)\psi_b e^{-iE_b t/\hbar} \quad (3.82)$$

Now we solve for $c_a(t)$ and $c_b(t)$ by using the time-dependent Schrodinger equation,

$$H\Psi = i\hbar\frac{\partial\Psi}{\partial t}, \text{ where } H = H_0 + H'(t) \quad (3.83)$$

Then we see that,

$$\begin{aligned} c_a[H_0\psi_a]_e^{-iE_at/\hbar} + c_b[H_0\psi_b]e^{-iE_bt/\hbar} + c_a[H'\psi_a]_e^{-iE_at/\hbar} \\ + c_b[H'\psi_b]e^{-iE_bt/\hbar} = i\hbar[\dot{c}_a\psi_a e^{-iE_at/\hbar} \dot{c}_b\psi_b e^{-iE_bt/\hbar} \\ + c_a\psi_a \left(\frac{iE_a}{\hbar}\right) e^{-iE_at/\hbar} + c_b\psi_b \left(\frac{iE_b}{\hbar}\right) e^{-iE_bt/\hbar}] \end{aligned} \quad (3.84)$$

This then simplifies to,

$$c_a[H'\psi_a]_e^{-iE_at/\hbar} + c_b[H'\psi_b]e^{-iE_bt/\hbar} = i\hbar[\dot{c}_a\psi_a e^{-iE_at/\hbar} \dot{c}_b\psi_b e^{-iE_bt/\hbar} \quad (3.85)$$

We isolate \dot{c}_a by taking the inner product with ψ_a and exploiting the orthogonality of ψ_a and ψ_b .

$$c_a\langle\psi_a|H'|\psi_a\rangle_e^{-iE_at/\hbar} + c_b\langle\psi_a|H'|\psi_b\rangle e^{-iE_bt/\hbar} = i\hbar\dot{c}_a e^{-iE_at/\hbar} \quad (3.86)$$

Then we define,

$$H'_{ij} \equiv \langle\psi_i|H'|\psi_j\rangle \quad (3.87)$$

The hermiticity of H' says that $H'_{ji} = (H'_{ij})^*$. Now multiplying with $-(i/\hbar)e^{iE_at/\hbar}$, we conclude that,

$$\dot{c}_a = -\frac{i}{\hbar}[c_a H'_{aa} + c_b H'_{ab} e^{-i(E_b - E_a)t/\hbar}] \quad (3.88)$$

Similarly the inner product with ψ_b isolate \dot{c}_b and gives the result,

$$\dot{c}_b = \frac{i}{\hbar}[c_b H'_{bb} + c_a H'_{ba} e^{-i(E_b - E_a)t/\hbar}] \quad (3.89)$$

Equations (15) and (16) are equivalent to the time-dependent Schrodinger equation for a two level system. And the diagonal matrix elements of H' vanish giving,

$$H'_{aa} = H'_{bb} = 0 \quad (3.90)$$

And the equations simplify to,

$$\dot{c}_a = -\frac{i}{\hbar}H'_{ab}e^{-i\omega_0 t}c_b \quad (3.91)$$

$$\dot{c}_b = -\frac{i}{\hbar}H'_{ab}e^{i\omega_0 t}c_a \quad (3.92)$$

Where,

$$\omega_0 = \frac{E_b - E_a}{\hbar}$$

3.6.3 Time-Dependent Perturbation Theory

Defining a size for the perturbation H' , considering it to be small, we can obtain solutions for equations (18) and (19) by the process of successive approximations.

Suppose the particle starts out in the lower state,

$$c_a(0) = 1. \quad c_b(0) = 0 \quad (3.93)$$

If there exists no perturbation, these states remain like this forever.

Zeroth Order:

$$c_a^{(0)}(t) = 1 \quad c_b^{(0)}(t) = 0 \quad (3.94)$$

To calculate the first-order approximation, we insert these values on the right side of equations (18) and (19)

First Order:

$$\begin{aligned} \frac{dc_a}{dt} &= 0 \rightarrow c_a^{(1)}(t) = 1; \\ \frac{dc_b}{dt} &= -\frac{i}{\hbar} H'_{ba} e^{i\omega_0 t} \rightarrow c_b^{(1)} = \frac{i}{\hbar} \int_0^t H'_{ba}(t') e^{i\omega_0 t'} dt' \end{aligned} \quad (3.95)$$

Second Order:

$$\begin{aligned} \frac{dc_a}{dt} &= -\frac{i}{\hbar} H'_{ba} e^{i\omega_0 t} \left(\frac{i}{\hbar} \right) \int_0^t H'_{ba}(t') e^{i\omega_0 t'} dt' \rightarrow \\ c_a^{(2)}(t) &= 1 - \frac{1}{\hbar} \int_0^t H'_{ab}(t') e^{i\omega_0 t'} \left[\int_0^{t'} H'_{ba}(t'') e^{i\omega_0 t''} dt'' \right] dt' \end{aligned} \quad (3.96)$$

We can continue this process for obtaining n-order approximations.

3.6.4 Sinusoidal Perturbations

If the perturbation has sinusoidal time dependence,

$$H'(r, t) = V(r) \cos(\omega t) \quad (3.97)$$

so that,

$$H'_{ab} = V_{ab} \cos(\omega t) \quad (3.98)$$

Where,

$$V_{ab} \equiv \langle \psi_a | V | \psi_b \rangle \quad (3.99)$$

For the first order perturbations, using equation (22),

$$c_b(t) \approx -\frac{i}{\hbar} \int_0^t \cos(\omega t') dt' = -\frac{iV_{ba}}{2\hbar} \int_0^t \left[e^{i(\omega_0+\omega)t'} + e^{i(\omega_0-\omega)t'} \right] dt' \quad (3.100)$$

$$= -\frac{V_{ba}}{2\hbar} \left[\frac{e^{i(\omega_0+\omega)t} - 1}{\omega_0 + \omega} + \frac{e^{i(\omega_0-\omega)t} - 1}{\omega_0 - \omega} \right] \quad (3.101)$$

Simplifying this equation by restricting our attention to driving frequency ω close to transition frequency ω_0 , the second term dominates. To be more specific, we assume,

$$\omega_0 + \omega \gg |\omega_0 - \omega| \quad (3.102)$$

Perturbation at other frequencies have negligible probability for causing a transition, so this isn't a limitation. Now the equation simplifies to,

$$\begin{aligned} c_b(t) &\approx -\frac{V_{ba}}{2\hbar} \frac{e^{i(\omega_0-\omega)t} - 1}{\omega_0 - \omega} [e^{i(\omega_0-\omega)t/2} - e^{-i(\omega_0-\omega)t/2}] \\ &= -i \frac{V_{ba}}{\hbar} \frac{\sin[(\omega_0 - \omega)t/2]}{\omega_0 - \omega} e^{i(\omega_0-\omega)t/2} \end{aligned} \quad (3.103)$$

The transition probability, the probability that a particle which started out in the state ψ_a will be found at a time t , in the state ψ_b is,

$$P_{a \rightarrow b}(t) = |c_b(t)|^2 \approx \frac{|V_{ba}|^2}{\hbar^2} \frac{\sin^2[(\omega_0 - \omega)t/2]}{(\omega_0 - \omega)^2} \quad (3.104)$$

3.7 Emission and Absorption of Radiation

3.7.1 Electromagnetic Waves

An atom, in the presence of a passing light wave, responds to the electric component. It is sinusoidal in nature,

$$E = E_0 \cos(\omega t) \hat{k} \quad (3.105)$$

Where q is the charge of the electron. Evidently,

$$H'_{ba} = -q E_0 \cos(\omega t), \quad q \equiv q \langle \psi_b | z | \psi_a \rangle \quad (3.106)$$

When ψ is an even or odd function of z , $z|\psi|^2$ is odd and integrates to zero, hence the diagonal matrix elements of H' vanish, hence the perturbation is oscillatory and is of the form,

$$V_{ba} = -q E_0 \quad (3.107)$$

3.7.2 Absorption, stimulated emission and spontaneous emission

If an atom starts in the lower state ψ_a and you shine a polarized monochromatic beam of light on it, the probability of a transition to the "upper" state ψ_b is given by,

$$P_{a \rightarrow b}(t) = \left(\frac{\mathcal{E} E_0}{\hbar} \right)^2 \frac{\sin^2[(\omega_0 - \omega)t/2]}{(\omega_0 - \omega)^2} \quad (3.108)$$

The atom absorbs an energy of $E_b - E_a = \hbar\omega_0$ from the electromagnetic field. We could say that it has absorbed a photon.

Now doing the same derivation for the transition from lower to upper state, we get

$$P_{b \rightarrow a}(t) = \left(\frac{\mathcal{E} E_0}{\hbar} \right)^2 \frac{\sin^2[(\omega_0 - \omega)t/2]}{(\omega_0 - \omega)^2} \quad (3.109)$$

Here we note that the probability of transition from $a \rightarrow b$ is the same as $b \rightarrow a$, and this was called stimulated emission. The electromagnetic field gains energy $\hbar\omega_0$ from the atom.

Spontaneous emission is when an atom in the excited state makes a transition downward with a release of a photon without the application of any electromagnetic field.

3.7.3 Incoherent perturbations

The energy density of an electromagnetic wave is,

$$u = \frac{\epsilon_0}{2} E_0^2 \quad (3.110)$$

The transition probability is proportional to the energy density of the fields,

$$P_{b \rightarrow a}(t) = \frac{2u}{\epsilon_0 \hbar^2} |\mathcal{E}|^2 \frac{\sin^2[(\omega_0 - \omega)t/2]}{(\omega_0 - \omega)^2} \quad (3.111)$$

But this is for a monochromatic perturbation for a single frequency ω , now subjecting the system to a range of frequencies, $u \rightarrow \rho(\omega)d\omega$ where $\rho(\omega)d\omega$ is the energy density in the frequency range $d\omega$ and the net transition probability takes the form of an integral,

$$P_{b \rightarrow a}(t) = \frac{2}{\epsilon_0 \hbar^2} |\mathcal{E}|^2 \int_0^\infty \rho(\omega) \left\{ \frac{\sin^2[(\omega_0 - \omega)t/2]}{(\omega_0 - \omega)^2} \right\} d\omega \quad (3.112)$$

The term in the curly brackets is sharply peaked about ω_0 . while $\rho(\omega)$ is relatively broad, so we replace $\rho(\omega)$ with $\rho(\omega_0)$ and take it outside the integral,

$$P_{b \rightarrow a}(t) \approx \frac{2|\wp|^2}{\epsilon_0 \hbar^2} \rho(\omega_0) \int_0^\infty \left\{ \frac{\sin^2[(\omega_0 - \omega)t/2]}{(\omega_0 - \omega)^2} \right\} d\omega \quad (3.113)$$

Changing variables from $x \equiv (\omega_0 - \omega)t/2$, extending the limits of integration to $x = \pm\infty$, looking up the definite integral,

$$\int_{-\infty}^{\infty} \frac{\sin^2 x}{x^2} dx = \pi$$

we find that,

$$P_{b \rightarrow a}(t) \approx \frac{\pi |\wp|^2}{\epsilon_0 \hbar^2} \rho(\omega_0) t \quad (3.114)$$

The transition probability is proportional to t . The flopping phenomenon characteristic of a monochromatic perturbation gets washed out when we hit the system with an incoherent spread of frequencies. The transition rate is now a constant,

$$R_{b \rightarrow a} = \frac{\pi}{\epsilon_0 \hbar} |\wp|^2 \rho(\omega_0) \quad (3.115)$$

We take all possible polarisations and not only from x and z directions, hence instead of $|\wp|^2$, we have an average $|\hat{n} \cdot \wp|^2$, where

$$\wp = q \langle \psi_b | r | \psi_a \rangle \quad (3.116)$$

And the average is over both polarisations and over all incident directions. This averaging is carried out as follows,

Polarisation: For propagation in the z-direction, the two possible polarisations are \hat{i} and \hat{j} , so the polarisation average (p) is,

$$(\hat{n} \cdot \wp)_p^2 = \frac{1}{2} [(\hat{i} \cdot \wp)^2 + (\hat{j} \cdot \wp)^2] = \frac{1}{2} \wp^2 \sin^2 \theta \quad (3.117)$$

Where θ is the angle between \wp and the direction of propagation.

Propagation direction: Setting the polar axis along \wp and integrate over all propagation directions to get the polarisation-propagation average,

$$(\hat{n} \cdot \wp)_{p\theta}^2 = \frac{1}{4\pi} \int \left[\frac{1}{2} \wp^2 \sin^2 \theta \right] \sin \theta d\theta d\phi = \frac{\wp^2}{4} \int_0^\pi \sin^3 \theta d\theta = \frac{\wp^3}{3} \quad (3.118)$$

So the transition rate for the stimulated emission from state b to state a , under the influence of incoherent, unpolarized light incident from all directions, is,

$$R_{b \rightarrow a} = \frac{\pi}{3\epsilon_0 \hbar^2} |\wp|^2 \rho(\omega_0) \quad (3.119)$$

Where \wp is the matrix element of the electric dipole moment between the two state and $\rho(\omega_0)$ is the energy density in the fields, per unit frequency, evaluated at $\omega_0 = (E_b - E_a)/\hbar$.

3.8 Spontaneous Emission

3.8.1 Einstein's A and B coefficients

Picture a container of atoms, N_a of them in a lower state ψ_a and N_b of them in the upper state ψ_b . Let A be the spontaneous emission rate, so that the number of particle leaving the upper state by this process per unit time is $N_b A$. The transition rate for stimulated emission is proportional to the energy density of the electromagnetic field. The number of upper state particles leaving is also similarly found. The absorption rate is proportional to $\rho(\omega_0)$. Now,

$$\frac{dN_b}{dt} = -N_b A - N_b B_{ba} \rho(\omega_0) + N_a B_{ab} \rho(\omega_0) \quad (3.120)$$

Supposing that the atoms are in thermal equilibrium with the ambient field so that the number of particles in each level is constant. $dN_b/dt = 0$, hence,

$$\rho(\omega_0) = \frac{A}{(N_a/N_b)B_{ab} - B_{ba}} \quad (3.121)$$

From statistical mechanics, the number of particles with energy E . in thermal equilibrium at temperature T , is proportional to the Boltzmann factor, $e^{-E/k_b T}$, so

$$\frac{N_a}{N_b} = \frac{e^{-E_a/k_b T}}{e^{-E_b/k_b T}} = e^{\hbar\omega_0/k_b T} \quad (3.122)$$

and hence,

$$\rho(\omega_0) = \frac{A}{e^{\hbar\omega_0/k_b T} B_{ab} - B_{ba}} \quad (3.123)$$

From Planck's blackbody formula,

$$\rho(\omega) = \frac{\hbar}{\pi^2 c^3} \frac{\omega^3}{e^{\hbar\omega/k_b T} - 1} \quad (3.124)$$

And from these two equations we can deduce that,

$$B_{ab} = B_{ba} \quad (3.125)$$

And so,

$$A = \frac{\omega^3 \hbar}{\pi^2 c^3} B_{ba} \quad (3.126)$$

We see that from equation (52), that the transition rate for stimulated emission is the same as for absorption. Now, we deduce from equation (46) that,

$$B_{ba} = \frac{\pi^2 c^3}{\omega^3 \hbar} |\wp|^2 \quad (3.127)$$

And spontaneous emission rate is,

$$A = \frac{\omega^3 |\wp|^2}{3\pi \epsilon_0 \hbar c^3} \quad (3.128)$$

3.8.2 The lifetime of an excited state

Suppose that you have a bottle full of atoms, with $N_b(t)$ of them in the excited stat. Due to spontaneous emission, this number decreases as time goes on, and to be more specifi, in a time interval dt you will lose a fraction of $A dt$ of them,

$$dN_b = -AN_b dt \quad (3.129)$$

Solving for $N_b(t)$, we get,

$$N_B(t) = N_b(0)e^{-At} \quad (3.130)$$

Here we can see that the number remaining in the excited state decreases exponentially, with a time constant,

$$\tau = \frac{1}{A} \quad (3.131)$$

We call this the lifetime of a state, or to be more technical, it is the time taken for $N_B(t)$ to reach $1/e \approx 0.368$ of its initial value.

Suppose that there are many more states, and many more decays, the transition rates add up, and the net lifetime is,

$$\tau = \frac{1}{A_1 + A_2 + A_3 + \dots} \quad (3.132)$$

3.8.3 Selection rules

The calculation of spontaneous emission rates are reduced to a matter of evaluating matrix elements of the form,

$$\langle \psi_b | \mathbf{r} | \psi_a \rangle$$

Specifying the states with quantum numbers n , l and m ,

$$\langle b'l'm' | \mathbf{r} | nlm \rangle \quad (3.133)$$

Exploitation of the angular momentum commutation relations and the hermiticity of the angular momentum operators yield these constraints on this quantity,

Selection rules involving m and m' : No transitions occur unless $\Delta m = +_1$ or 0

Selection rules involving l and l' : No transitions occur unless $\Delta l = +_1$

Chapter 4

Scattering

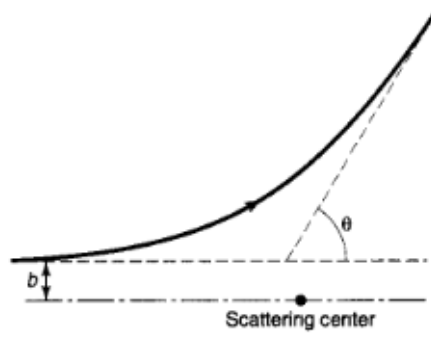
4.1 Classical Scattering

4.1.1 Motivation

We can also define the size/radius of the proton is through its rate of interacting with itself or other particles. This is done by us determining the cross-sectional area. The larger this area is, the more likely it is that you will interact with it. The smaller the area, the less likely to interact. This motivates a connection between proton size and scattering probability. In particle physics, a collision or interaction rate is expressed in effective cross-sectional area, typically just called cross section. As an “area,” we can measure scattering cross sections as the square of some relevant length scale.

4.1.2 The problem

Consider a particle incident on some scattering center. It comes in with an energy E and an impact parameter b , and it emerges at some scattering angle θ . The essential problem of classical scattering theory is this: *Given the impact parameter, calculate the scattering angle.* Ordinarily, of course, the smaller the impact parameter, the greater the scattering angle.



4.1.3 Solving for differential cross-section

Particles incident within an infinitesimal patch of cross-sectional area $d\sigma$ will scatter into a corresponding infinitesimal solid angle $d\Omega$. The larger $d\sigma$ is, the bigger $d\Omega$ will be; the proportionality factor, $D(\theta) = d\sigma/d\Omega$, is called the differential (scattering) cross-section, and is given by,

$$d\sigma = D(\theta)d\Omega \quad (4.1)$$

In terms of the impact parameter and the azimuthal angle ϕ , $d\sigma = b.db.d\phi$ and $d\Omega = \sin(\theta)d\theta d\phi$, and so,

$$D(\theta) = \frac{b}{\sin \theta} \left| \frac{db}{d\theta} \right| \quad (4.2)$$

And then the total cross-section is the integral of $D(\theta)$ over all solid angles,

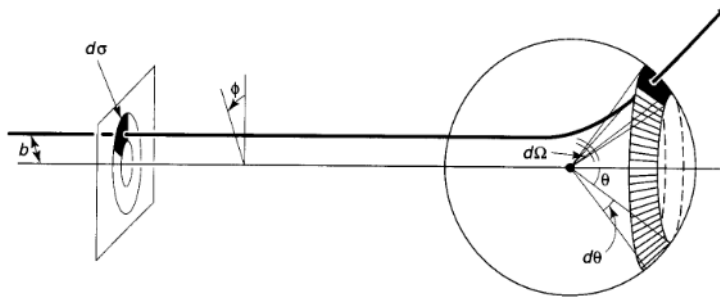
$$\sigma = \int D(\theta)d\Omega \quad (4.3)$$

The differential cross-section is the total area of incident beam that is scattered by the target. Beams incident within this area will hit the target, and those farther out will miss it completely.

If we have a beam of incident particles, with uniform intensity/luminosity (\mathcal{L}), the number of particles entering area $d\sigma$ (and hence scattering into solid angle $d\Omega$), per unit time, is $dN = \mathcal{L}d\sigma = \mathcal{L}D(\theta)d\Omega$, then,

$$D(\theta) = \frac{1}{\mathcal{L}} \frac{dN}{d\Omega} \quad (4.4)$$

This is the definition of the differential cross-section.



4.2 Quantum Scattering

4.2.1 Defining the problem

In the quantum theory of scattering, we imagine an incident plane wave, $\psi(z) = Ae^{ikz}$, traveling in the z direction, which encounters a scattering potential, producing an outgoing spherical wave. That is, we look for solutions to the Schrödinger equation of the generic form,

$$\psi(r, \theta) \approx A \left\{ e^{ikz} + f(\theta) \frac{e^{ikr}}{r} \right\}, \text{ for large } r \quad (4.5)$$

The relation between wave number k and energy of incident particles are,

$$k \equiv \frac{\sqrt{2mE}}{\hbar} \quad (4.6)$$

4.2.2 Determining scattering amplitude

Probability of the incident particle travelling with speed v passing through infinitesimal area $d\sigma$ in time dt is,

$$dP = |\psi_{incident}|^2 dV = |A|^2 (vdt) d\sigma \quad (4.7)$$

This is equal to the probability that the particle later emerges into the corresponding solid angle $d\Omega$,

$$dP = |\psi_{scattered}|^2 dV = \frac{|A|^2 |f|^2}{r^2} (vdt) r^2 d\sigma \quad (4.8)$$

And $d\sigma = |f|^2 d\Omega$, so,

$$D(\theta) = \frac{d\sigma}{d\Omega} = |f(\theta)|^2 \quad (4.9)$$

The differential cross-section (which is the quantity of interest to the experimentalist) is equal to the absolute square of the scattering amplitude. Now we look at different methods to determine this scattering amplitude.

4.3 Partial Wave Analysis

4.3.1 Formalism

We know that the Schrodinger equation for a spherically symmetrical potential $V(r)$ admits the separable solutions,

$$\psi(r, \theta, \phi) = R(r) Y_l^m(\theta, \phi) \quad (4.10)$$

Where Y_l^m is a spherical harmonic and $u(R) = rR(r)$ satisfies the radial equation,

$$-\frac{\hbar^2}{2m} \frac{d^2 u}{dr^2} + \left[V(r) + \frac{\hbar^2}{2m} \frac{l(l+1)}{r^2} \right] u = Eu \quad (4.11)$$

At very large r , the potential goes to zero, and the centrifugal term is negligible, so,

$$\frac{d^2 u}{dr^2} \approx -k^2 u \quad (4.12)$$

Whose general solution is takes the form,

$$u(r) = C e^{ikr} + D e^{-ikr} \quad (4.13)$$

The first term represents an outgoing spherical wave, and the second an incoming one. For the scattered wave, we want $D = 0$. At very large r , then.

$$R(r) \approx \frac{e^{ikr}}{r} \quad (4.14)$$

The radial equation then becomes,

$$\frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} u = -k^2 u \quad (4.15)$$

The general solution for the radial equation is a linear combinations of spherical Bessel functions,

$$u(r) = A r j_l(kr) + B r n_l(kr) \quad (4.16)$$

We need solutions that are linear combinations analogous to e^{ikr} and e^{-ikr} , these are called the spherical Hankel functions,

$$h_l^{(1)} \equiv j_l(x) + i n_l(x) \quad (4.17)$$

Below we see some examples of Hankel functions,

$$\begin{array}{ll}
 h_0^{(1)} = -i \frac{e^{ix}}{x} & h_0^{(2)} = i \frac{e^{-ix}}{x} \\
 h_1^{(1)} = \left(-\frac{i}{x^2} - \frac{1}{x} \right) e^{ix} & h_1^{(2)} = \left(\frac{i}{x^2} - \frac{1}{x} \right) e^{-ix} \\
 h_2^{(1)} = \left(-\frac{3i}{x^3} - \frac{3}{x^2} + \frac{i}{x} \right) e^{ix} & h_2^{(2)} = \left(\frac{3i}{x^3} - \frac{3}{x^2} - \frac{i}{x} \right) e^{-ix} \\
 \left. \begin{array}{l} h_\ell^{(1)} \rightarrow \frac{1}{x} (-i)^{\ell+1} e^{ix} \\ h_\ell^{(2)} \rightarrow \frac{1}{x} (i)^{\ell+1} e^{-ix} \end{array} \right\} \text{for } x \gg 1
 \end{array}$$

The Hankel function of the first kind becomes e^{-ikr}/r for large r , so we use these to get,

$$R(r) = C j_l^{(1)}(kr) \quad (4.18)$$

4.3.2 Exact wavefunction and the partial wave amplitude

The exact wave function in the exterior region where $V(r) = 0$ is,

$$\psi(r, \theta, \phi) = A \left\{ e^{ikz} + f(\theta, \phi) \frac{e^{ikr}}{r} \right\} \quad (4.19)$$

Where,

$$f(\theta, \phi) + \frac{1}{k} \sum_{l,m} (-i)^{l+1} C_{l,m} Y_l^m(\theta, \phi) \quad (4.20)$$

The $C_{l,m}$ are called the partial wave amplitudes. Now the cross section is,

$$D(\theta, \phi) = |f(\theta, \phi)|^2 = \frac{1}{k^2} \sum_{l,m} \sum_{l',m'} (i)^{l-l'} C_{l,m}^* C_{l',m'} (Y_l^m)^* Y_{l'}^{m'} \quad (4.21)$$

And the total cross-section is,

$$\sigma = \frac{1}{k^2} \sum_{l,m} \sum_{l',m'} (i)^{l-l'} C_{l,m}^* C_{l',m'} \int (Y_l^m)^* Y_{l'}^{m'} d\Omega = \frac{1}{k^2} \sum_{l,m} |C_{l,m}|^2 \quad (4.22)$$

We know from the Legendre functions that,

$$Y_l^0(\theta, \phi) = \sqrt{\frac{2l+1}{4\pi}} P_l(\cos\theta) \quad (4.23)$$

where P_l is the l th Legendre Polynomial. Now the exact wave function in the exterior region is,

$$\psi(r, \theta) = A \left\{ e^{ikz} + \sum_{l=0}^{\infty} \sqrt{\frac{2l+1}{4\pi}} C_l h_l^{(1)}(kr) P_l(\cos\theta) \right\} \quad (4.24)$$

The scattering amplitude is now given by,

$$f(\theta) = \frac{1}{k} \sum_{l=0}^{\infty} (-i)^{l+1} \sqrt{\frac{2l+1}{4\pi}} C_l P_l(\cos\theta) \quad (4.25)$$

and the total cross-section is,

$$\sigma = \frac{1}{k^2} \sum_{l=0}^{\infty} |C_l|^2 \quad (4.26)$$

To fix the hybrid notation of the cartesian incoming wave and the spherical outgoing wave, we write it in a more consistent form.

We know that the general solution to the Schrodinger equation with $V = 0$ can be written in the form,

$$\sum_{l,m} [A_{l,m} j_l(kr) + B_{l,m} n_l(kr)] Y_l^m(\theta, \phi) \quad (4.27)$$

Expanding the plane wave in terms of spherical waves using Rayleigh's formula,

$$e^{ikz} = \sum_{l=0}^{\infty} i^l (2l+1) j_l(kr) P_l(\cos\theta) \quad (4.28)$$

Substituting this in Equation (24), the consistent exterior region wave function can be written as,

$$\psi(r, \theta) = A \left[l(2l+1) j_l(kr) + \sum_{l=0}^{\infty} \sqrt{\frac{2l+1}{4\pi}} C_l h_l^{(1)}(kr) \right] P_l(\cos\theta) \quad (4.29)$$

4.4 Phase Shift

Let's begin by considering a one-dimensional scattering problem with a localized potential on the half-line $x < 0$ and a brick wall at $x = 0$. So a wave incident from the left,

$$\psi_i(x) = Ae^{ikx} \quad (4.30)$$

is entirely reflected,

$$\psi_r(x) = Be^{-ikx} \quad (4.31)$$

where $x < -a$. No matter what happens in $-a < x < 0$ (the interaction

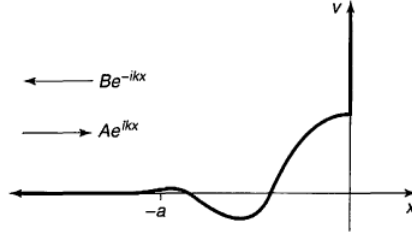


Figure 4.1: 1D scattering from a localized potential bounded on the right by an infinite wall

region), the amplitude (amplitude in the context of waves not probability amplitude) of the reflected wave is the same as the incident wave simply due to conservation of probability. However, the two waves need not have the same phase. If there were no potential at all ($V(x) = 0$), but just at the wall ($x = 0$), then $B = -A$, since the total wave function, incident + reflected must vanish at the origin,

$$\psi_0 = A(e^{ikx} - e^{-ikx}) \quad (4.32)$$

If the potential is not zero ($V(x) \neq 0$), then the wave function ($x < -a$) takes the form:

$$\psi = A(e^{ikx} - e^{i(2\delta - kx)}) \quad (4.33)$$

Thus, the whole scattering problem reduces to the problem of calculating the phase shift δ as a function of k and hence of the Energy $E = \hbar^2 k^2 / 2m$. Yes there's a factor of 2, before δ , but that's only conventional. We think of the incident wave as being phase shifted once on the way in and again on the way out. Thus, by δ we mean the one-way phase shift and 2δ the total phase shift. We go about this by solving the Schrodinger equation in $-a < x < 0$ along with relevant boundary conditions. Why are we working with δ rather than the complex amplitude B ? It makes the physics and math simpler:

- **Physically:** We only need to think of the conservation of probability. The potential merely shifts the phase
- **Mathematically:** We trade a complex number for a real one

Let's return to the 3D case. The incident plane wave carries no angular momentum in the z direction. Thus Rayleigh's formula contains no terms with $m \neq 0$ but instead it contains all values of the total angular momentum ($l = 0, 1, 2$). Since angular momentum is conserved by a spherically symmetric potential each partial wave labelled by a particular l scatters independently with no change in amplitude (amplitude in this context refer to the amplitude of the wave not the probability amplitude) but differing in phase. If there is no potential then $\psi_0 = Ae^{ikx}$ and the l th partial wave is

$$\psi_0^l = Ai^l(2l+1)j_l(kr)P_l(\cos(\theta)) \quad (4.34)$$

But from our previous considerations,

$$j_l(x) = \frac{1}{2} [h^{(1)}(x) + h_l^2(x)] \approx \frac{1}{2x} [(-i)^{l+1}e^{ix} + i^{l+1}e^{-ix}] \quad (4.35)$$

for $x \gg 1$. So for large r ,

$$\psi_0^{(l)} \approx A \frac{2l+1}{2ikr} [e^{ikr} - (-1)^l e^{-ikr}] P_l(\cos(\theta)) \quad (4.36)$$

The second term in square brackets corresponds to an incoming spherical wave. It is unchanged when we introduce the scattering potential. The first term is the outgoing wave. It picks up a phase shift δ_l :

$$\psi^{(l)} \approx A \frac{2l+1}{2ikr} [e^{i(kr+2\delta_l)} - (-1)^l e^{-ikr}] P_l(\cos(\theta)) \quad (4.37)$$

Think of it as a converging spherical wave due to the $h_l^{(2)}$ component in e^{ikz} , which is phase shifted by $2\delta_l$ and emerges as an outgoing spherical wave i.e. the h_l^l part of e^{ikz} as well as the scattered wave itself. In the previous section the whole theory was expressed in terms of partial wave amplitudes a_l , now we have formulated it in terms of the phase shifts δ_l . There must be a connection between the two. Well if we take the asymptotic i.e. large r limit of eq. (4.37):

$$\psi^{(l)} \approx A \left(\frac{(2l+1)}{2ikr} [e^{i(kr+2\delta_l)} - (-1)^l e^{-ikr}] + \frac{(2l+1)}{r} a_l e^{ikr} \right) P_l(\cos(\theta)) \quad (4.38)$$

With the generic expression in terms of $e^{i\delta_l}$ we find

$$a = \frac{1}{2ik}(e^{2i\delta_l} - 1) = \frac{1}{k}e^{i\delta_l} \sin(\delta_l) \quad (4.39)$$

Although we used the asymptotic form of the wave function to find the connection there's nothing approximate about the result. Both of them are constants independent of r and δ_l means the phase shift in the asymptotic region i.e. where the Hankel functions have settled down to $e^{\pm ikr}/kr$. It follows in particular that,

$$f(\theta) = \frac{1}{k} \sum_{l=0}^{\infty} (2l+1) e^{i\delta_l} \sin(\delta_l) P_l(\cos(\theta)) \quad (4.40)$$

and,

$$\sigma = \frac{4\pi}{k^2} \sum_{l=0}^{\infty} (2l+1) \sin^2(\delta_l) \quad (4.41)$$

Voila!

4.5 Born Approximation

4.5.1 Integral Form of the Schrodinger Equation

Before we even head to deriving the "Integral Form of the Schrodinger Equation". Why you might ask? It will become evident in the upcoming sections. So let's begin by recalling the time-independent Schrodinger equation

$$\frac{\hbar^2 \nabla^2 \psi}{2m} + V\psi = E\psi \quad (4.42)$$

We can rewrite this as,

$$(\nabla^2 + k^2)\psi = Q \quad (4.43)$$

where

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

$$Q = \frac{2m}{\hbar^2} V\psi$$

This looks pretty similar to the Helmholtz equation from electrodynamics. Here however the "inhomogeneous" term Q itself depends on ψ . Suppose we could find a function that solves the Helmholtz equation with a delta function source:

$$(\nabla^2 + k^2)G(\vec{r}) = \delta^3(\vec{r}) \quad (4.44)$$

We can then express as an integral:

$$\psi(\vec{r}) = \int G(\vec{r} - \vec{r}_0) Q(\vec{r}_0) d^3 \vec{r}_0 \quad (4.45)$$

$G(\vec{r})$ is called the Green's function for the Helmholtz equation. Moreover, generally speaking the Green's function for a linear differential equation represents the response to a delta function. Our goal now is to solve this differential equation, we start by Fourier transforming it to turn it into an algebraic equation:

$$G(\vec{r}) = \frac{1}{(2\pi)^{3/2}} \int e^{i\vec{s} \cdot \vec{r}} g(\vec{s}) d^3 \vec{s} \quad (4.46)$$

Then,

$$(\nabla^2 + k^2)G(\vec{r}) = \frac{1}{(2\pi)^{3/2}} (\nabla^2 + k^2) \int e^{i\vec{s} \cdot \vec{r}} g(\vec{s}) d^3 \vec{s}$$

But,

$$\nabla^2 e^{i\vec{s} \cdot \vec{r}} = -s^2 e^{i\vec{s} \cdot \vec{r}}$$

and

$$\delta^3(\vec{r}) = \frac{1}{(2\pi)^{3/2}} \int e^{i\vec{s} \cdot \vec{r}} g(\vec{s}) d^3 \vec{s}$$

thus,

$$\frac{1}{(2\pi)^{3/2}} \int (-s^2 + k^2) e^{i\vec{s} \cdot \vec{r}} g(\vec{s}) d^3 \vec{s} = \frac{1}{(2\pi)^3} \int e^{i\vec{s} \cdot \vec{r}} d^3 \vec{s}$$

It follows from Plancherel's theorem that,

$$g(\vec{s}) = \frac{1}{(2\pi)^{3/2} (k^2 - s^2)}$$

Plugging this back, we see that

$$G(\vec{r}) = \frac{1}{(2\pi)^3} \int e^{i\vec{s} \cdot \vec{r}} \frac{1}{(k^2 - s^2)} d^3 \vec{s}$$

We now switch coordinates for convenience. Now \vec{r} is fixed as far as the s integration matters so we'll choose spherical coordinates with the polar axis along \vec{r} . Then

$$\int_0^\pi e^{isr \sin(\theta)} \sin(\theta) d\theta = -\frac{e^{isr \cos(\theta)}}{isr} \Big|_0^\pi = \frac{2 \sin(sr)}{sr}$$

We can represent this visually as,

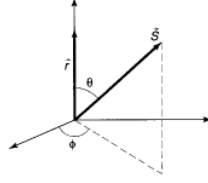


Figure 4.2: New coordinates for the integral

Thus,

$$G(\vec{r}) = \frac{1}{(2\pi)^2} \frac{2}{r} \int_0^\infty \frac{s \sin(sr)}{k^2 - s^2} ds = \frac{1}{4\pi^2 r} \int_{-\infty}^\infty \frac{s \sin(sr)}{k^2 - s^2} ds$$

We can rewrite this as,

$$G(\vec{r}) = \frac{i}{8\pi^2 r} \left[\int_{-\infty}^\infty \frac{se^{isr}}{(s-k)(s+k)} ds - \int_{-\infty}^\infty \frac{se^{-isr}}{(s-k)(s+k)} ds \right] = \frac{i}{8\pi^2 r} (I_1 - I_2)$$

From Cauchy's integral formula it follows that,

$$I_1 = \oint \left[\frac{se^{isr}}{s+k} \right] \frac{1}{s-k} ds = 2\pi i \left[\frac{se^{isr}}{s+k} \right] \Big|_{s=k} = i\pi e^{ikr}$$

$$I_2 = \oint \left[\frac{se^{-isr}}{s-k} \right] \frac{1}{s+k} ds = -2\pi i \left[\frac{se^{-isr}}{s+k} \right] \Big|_{s=-k} = -i\pi e^{ikr}$$

Therefore,

$$G(\vec{r}) = \frac{i}{8\pi^2 r} [(i\pi e^{ikr}) - (-i\pi e^{ikr})] = -\frac{e^{ikr}}{4\pi r} \quad (4.47)$$

Note that $G + G_0$ still satisfies Equation (4.47). This is simply due to the multivalued nature of the holomorphic function. Thus, the integral form of the Schrodinger equation can be written as,

$$\psi(\vec{r}) = \psi_0(\vec{r}) - \frac{m}{2\pi\hbar^2} \int \frac{e^{ik|\vec{r}-\vec{r}_0|}}{|\vec{r}-\vec{r}_0|} V(\vec{r}_0) \psi(\vec{r}_0) d^3\vec{r}_0 \quad (4.48)$$

Let's see how this helps us.

4.5.2 The First Born Approximation

Suppose $V(\vec{r}_0)$ is localized about $\vec{r} = 0$, that is the potential drops to 0 after a finite region and we want to calculate $\psi(\vec{r})$ at points distant from the

scattering center. Then for all points that contribute to the integral form of the Schrodinger equation. So,

$$|\vec{r} - \vec{r}_0| = r^2 + r_0^2 - 2\vec{r}\vec{r}_0 \cong r^2 \left(1 - 2\frac{\vec{r} \cdot \vec{r}_0}{r^2}\right) \quad (4.49)$$

and hence,

$$|\vec{r} - \vec{r}_0| \cong r - \hat{r} \cdot \vec{r}_0 \quad (4.50)$$

Let,

$$\vec{K} = k\hat{z} \quad (4.51)$$

then

$$e^{-i\vec{K}|\vec{r}-\vec{r}_0|} \approx e^{ikr} e^{-i\vec{K} \cdot \vec{r}_0} \quad (4.52)$$

and therefore,

$$\frac{e^{-i\vec{K}|\vec{r}-\vec{r}_0|}}{|\vec{r} - \vec{r}_0|} \approx \frac{e^{ikr}}{r} e^{-i\vec{K} \cdot \vec{r}_0} \quad (4.53)$$

In the case of scattering, we want:

$$\psi_o(\vec{r}) = Ae^{ikz} \quad (4.54)$$

to represent an incident plane wave. For large r ,

$$\psi \cong Ae^{ikz} - \frac{m}{2\pi\hbar^2 A} \int e^{-i\vec{K} \cdot \vec{r}_0} V(\vec{r}_0) \psi(\vec{r}_0) d^3\vec{r}_0 \quad (4.55)$$

This is in the standard form. We can read off the scattering amplitude:

$$f(\theta, \phi) = \frac{m}{2\pi\hbar^2 A} \int e^{-i\vec{K} \cdot \vec{r}_0} V(\vec{r}_0) \psi(\vec{r}_0) d^3\vec{r}_0 \quad (4.56)$$

So far this is exact. Now we invoke the Born approximation: "Suppose the incoming plane wave is not substantially altered by the potential; then we can say that

$$\psi(\vec{r}_0) \cong \psi_0(\vec{r}_0) = Ae^{ikz_0} = Ae^{i\vec{K}' \cdot \vec{r}_0} \quad (4.57)$$

where

$$\vec{K}' = k\hat{z}$$

inside the integral. This would be just the wave function if V were zero. It is essentially just a weak potential approximation. Generally partial wave analysis is useful when the incident particle has low energy the only the first few terms in the series contribute significantly. The Born approximation applies when the potential is weak when compared to the incident energy, thus the deflection is small. In the Born approximation then,

$$f(\theta, \phi) \cong -\frac{m}{2\pi\hbar^2} \int e^{i(k' - k) \cdot \vec{r}_0} V(r_0) d^3\vec{r}_0 \quad (4.58)$$

In particular, for low energy scattering, the exponential factor is essentially constant over the scattering region and the Born approximation simplifies to:

$$f(\theta, \phi) \cong -\frac{m}{2\pi\hbar^2} \int V(\vec{r}) d^3r \quad (4.59)$$

For a spherically symmetrical potential, $V(\vec{r}) = V(r)$ but not necessarily at low energy. The Born approximation reduces to a simpler form. First we define:

$$\mathcal{K} = k' - k \quad (4.60)$$

and let the polar axis for the r_0 , the integral lies along so that;

$$(k' - k) \cdot r_0 = \mathcal{K} r_0 \cos(\theta_0) \quad (4.61)$$

Then,

$$f(\theta) \cong -\frac{m}{2\pi\hbar^2} \int e^{i\mathcal{K}r_0 \cos(\theta_0)} V(\theta_0) r_0^2 \sin(\theta_0) dr_0 d\theta_0 d\phi_0 \quad (4.62)$$

The integral is trivial, 2π , and the integral θ_0 is on we have encountered before in equation (). Dropping the subscript on r , we are left with

$$f(\theta) \cong -\frac{2m}{\hbar^2 \mathcal{K}} \int_0^\infty r V(r) \sin(\mathcal{K}r) dr \quad (4.63)$$

The angular dependence of f is carried by \mathcal{K} . From our previous considerations we can see that:

$$\mathcal{K} = 2k \sin(\theta/2) \quad (4.64)$$

4.5.3 Examples

Low-energy soft-sphere scattering

Note: We can't apply the Born approximation to hard-sphere scattering as the integral blows up due to our assumption (i.e. potential does not affect the wave function) here. Suppose,

$$V(\vec{r}) = \begin{cases} V_0, & \text{if } r \leq a \\ 0, & \text{if } r > a \end{cases} \quad (4.65)$$

In this case the low-energy scattering amplitude is,

$$f(\theta, \phi) \cong -\frac{m}{2\pi\hbar^2} V_0 \left(\frac{4}{3} \pi a^3 \right) \quad (4.66)$$

This is independent of θ and ϕ ! Thus, the differential cross-section is:

$$\frac{d\sigma}{d\Omega} = |f|^2 \cong \left[\frac{2mV_0a^3}{3\hbar^2} \right]^2 \quad (4.67)$$

and the total cross-section:

$$\sigma \cong 4\pi \left(\frac{2mV_0a^3}{3\hbar^2} \right)^2 \quad (4.68)$$

Yukawa Scattering

The Yukawa potential is a toy-model for the binding force in the nucleus of an atom. It has the form,

$$V(r) = \beta \frac{e^{-\mu r}}{r} \quad (4.69)$$

where β and μ are constants. The Born approximation gives,

$$f(\theta) \cong -\frac{2m\beta}{\hbar^2 k} \int_0^\infty e^{-\mu r} \sin(kr) dr = -\frac{2m\beta}{\hbar^2(\mu^2 + k^2)} \quad (4.70)$$

Rutherford Scattering

If we substitute $\beta = q_1 q_2 / 4\pi\epsilon_0$ and $\mu = 0$. The scattering amplitude is given by,

$$f(\theta) \cong -\frac{2mq_1q_2}{4\pi\epsilon_0\hbar^2k^2} \quad (4.71)$$

or,

$$f(\theta) \cong -\frac{q_1q_2}{16\pi\epsilon_0 E \sin^2(\theta/2)} \quad (4.72)$$

The differential cross-section is the square of this:

$$\frac{d\sigma}{d\Omega} = \left[\frac{q_1q_2}{16\pi\epsilon_0 E \sin^2(\theta/2)} \right]^2 \quad (4.73)$$

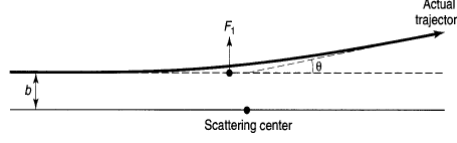


Figure 4.3: An example of the impulse approximation: the particle continues undeflected

4.5.4 The Born series

The Born approximation is very similar to the impulse approximation in the context of classical scattering. In that sector we start by assuming that the particle keeps going in a straight line and compute the transverse impulse that would be delivered to it in that case:

$$I = \int F_{\perp} dt \quad (4.74)$$

If the deflection is small in comparison to the motion, it would then be a good approximation to the transverse momentum supplied to the particle. Thus we express the scattering angle as:

$$\theta = \arctan(I/p) \quad (4.75)$$

where p is the incident momentum. This is the "first-order" impulse approximation. The zeroth-order is what we started with i.e. no deflection at all. Likewise, in the zeroth-order Born approximation the incident plane wave passes by with no modification and what we saw earlier was just the first order correction to this. But the same pattern of thought can lead us to a series which then leads us to higher-order corrections. Let's recall the integral form of the Schrodinger equation:

$$\psi(\vec{r}) = \psi_0(\vec{r}) + \int g(\vec{r} - \vec{r}_0) V(\vec{r}_0) \psi(\vec{r}_0) d^3 r_0 \quad (4.76)$$

where ψ_0 is the incident wave and,

$$g(\vec{r}) = -\frac{m}{2\pi\hbar^2} \frac{e^{ikr}}{r}$$

is the Green's function with a factor $m/2\pi\hbar^2$ for convenience and V is the scattering potential. Suppose we take the equation for ψ and plug it back into (4.76),

$$\psi = \psi_0 + \int gV\psi_0 + \int \int gVgV\psi$$

Iterating this we obtain the series expansion for ψ ,

$$\psi = \psi_0 + \int gV\psi_0 + \int \int gVgV\psi_0 + \int \int \int gVgVgV\psi_0 \dots \quad (4.77)$$

We notice the following from (4.77):

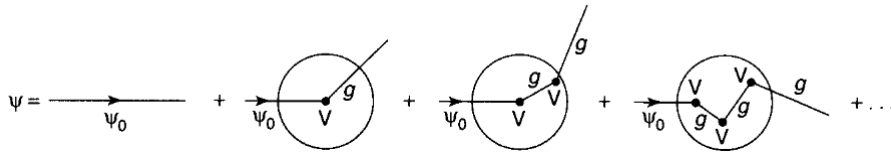


Figure 4.4: A diagram representing the Born series

- The first Born approximation truncates the series after the Next to Leading Order (NLO) term
- In the Leading Order ψ is untouched by V
- In the first order (Next to Leading Order) it is kicked once
- In the second order it is kicked, propagates to a new location and is kicked again and so on
- In this context the Green's function is essentially just the propagator ¹
- This was in fact the inspiration for Feynman diagrams which is expressed in terms of vertex factors (V) and propagators (g)

Figure (4.5.4) might look familiar, because it closely represents Feynman diagrams.

¹In this context it tells us how the disturbance propagates between one interaction and the next

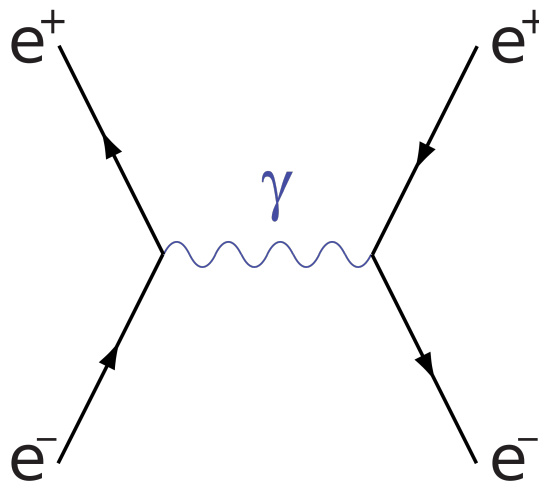


Figure 4.5: Bhabha scattering: Annihilation

Chapter 5

Path Integral Formulation

In this section we'll review the Path integral formulation, it's equivalence to the Schrodinger formalism and a toy model in this context.

5.1 The Path Integral Recepie

So far our strategy has been to find the eigenstates of H then express the propagator in terms of this. However, the path integral formulation cuts one step and gets to the propagator directly. For a single particle in one dimension we follow the following procedure to find $U(x, t; x', t')$:

1. Draw all paths in the $x - t$ plane connecting (x', t') and (x, t)
2. Find the action $S[x(t)]$ for each path $x(t)$
3. $U(x, t; x', t') = A \sum_{All\ paths} e^{i \frac{S[x(t)]}{\hbar}}$; where A is a normalization factor

Here we have in a sense that the classical path taken by the particle corresponds to the stationary path. This is analogous to the Lagrangian formulation of classical mechanics in contrast to the approaches we took earlier involving the Hamiltonian.

5.2 Equivalence to the Schrodinger Equation

In the Schrodinger formalism, the change in the state vector over an infinitesimal time ϵ in the position basis is:

$$\psi(x, \epsilon) - \psi(x, 0) = \frac{i\epsilon}{\hbar} \left[\frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x, 0) \right] \psi(x, 0) \quad (5.1)$$

to the first order in ϵ , the solution being

$$\psi(x, \epsilon) = \int_{-\infty}^{\infty} U(x, \epsilon; x') \psi(x', 0) dx' \quad (5.2)$$

This integral isn't so formidable as ϵ is simply just one slice in time.

$$\psi(x, \epsilon) = \left(\frac{m}{2\pi\hbar i\epsilon} \right)^{1/2} \int_{-\infty}^{\infty} \exp\left(\frac{im\eta^2}{2\hbar\epsilon} \right) \exp\left[-\left(\frac{i}{\hbar}\epsilon V\left(x + \frac{\eta}{2}, 0\right) \right) \right] \psi(x+\eta, 0) d\eta \quad (5.3)$$

Where, $\eta = x'$ Now, most of the contribution to the propagator must come from the stationary term, thus if we make the approximation

$$|\eta| \leq \left(\frac{2\epsilon\hbar\pi}{m} \right)^{1/2}$$

and Taylor expand while avoid the $\epsilon\eta$ terms and treating it to be a Gaussian integral we find that:

$$\psi(x, \epsilon) - \psi(x, 0) = \frac{i\epsilon}{\hbar} \left[\frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x, 0) \right] \psi(x, 0) \quad (5.4)$$

Which is exactly what we expect to see from the Schrodinger formalism as well.

5.3 Path Integral Evaluation of the Free-Particle Propagator

Let us consider the propagator. The problem is to solve for the integral

$$\int_{x_0}^{x_N} e^{iS[x(t)]/\hbar} \mathfrak{D}[x(t)] \quad (5.5)$$

where

$$\int_{x_0}^{x_N} \mathfrak{D}[x(t)]$$

is essentially the sum over all possible paths in configuration space. To do this we first express $x(t)$ with a discrete approximation which is accurate upto $N + 1$ points i.e. . The gaps between points are interpolated with straight lines. Now the naive hope is that when $N \rightarrow \infty$ the notion of the approximation disappears. Thus we will start by replacing,

$$S = \int_{t_0}^{t_N} \mathcal{L} dt = \int_{t_0}^{t_N} \frac{1}{2} m \dot{x}^2 dt \quad (5.6)$$

with,

$$S = \sum_{i=0}^{N-1} \frac{m}{2} \left(\frac{x_{i+1} - x_i}{\epsilon} \right)^2 \epsilon \quad (5.7)$$

where $x_i = x(t_i)$. Then integral then becomes,

$$U(x_N, t_N; x_0, t_0) = \int_{t_0}^{t_N} = \lim_{N \rightarrow \infty, \epsilon \rightarrow 0} A \int_{-\infty}^{\infty} \exp \left[\frac{i}{\hbar} \frac{m}{2} \sum_{i=0}^{N-1} \left(\frac{x_{i+1} - x_i}{\epsilon} \right)^2 \epsilon \right] \prod_{i=1}^{N-1} dx_i \quad (5.8)$$

Two assumptions are present here:

- t_N and t_0 have values that are implicitly defined
- The factor A is chosen so that we have the correct scale for U when

We can integrate by means of switching the variables up and then considering it to be a Gaussian integral. We then get

$$U = A \left(\frac{2\pi\hbar\epsilon i}{m} \right)^{N/2} \left(\frac{m}{2\pi\hbar i N \epsilon} \right)^{1/2} \exp \left[\frac{im(x_N - x_0)^2}{2\hbar N \epsilon} \right] \quad (5.9)$$

If we now let , we obtain the right result provided,

$$A = \left[\frac{2\pi\hbar\epsilon i}{m} \right]^{-N/2} = B^{-N}$$

This $1/B$ is in some senses the weighing function for each path. And thus we can understand how even though there are infinite paths, that only the stationary one is realized (because it has the highest weight) since it is most like the first order term. A similar idea is explored in the Born approximation section as well.

Chapter 6

Relativistic Quantum Mechanics

6.1 The Klein-Gordon Equation

In order to develop quantum mechanics relativistically, they started from the relativistic energy–momentum relation,

$$E^2 - |\vec{p}|^2 c^2 - m^2 c^4 = 0 \quad (6.1)$$

Substituting E and p for their respective operators,

$$E \Rightarrow i\hbar \frac{\partial}{\partial t}, \quad \vec{p} \Rightarrow -i\hbar \vec{\nabla},$$

and letting the equation act on a wavefunction $\phi(\vec{x}, t)$ the equation becomes,

$$\left(-\hbar^2 \frac{\partial^2}{\partial t^2} + \hbar^2 c^2 \nabla^2 - m^2 c^4 \right) \phi(\vec{x}, t) = 0 \quad (6.2)$$

This is the Klein-Gordon Equation. The wave function $\phi(\vec{x}, t)$ is also an object called a field because its arguments extend over all space and time. Another way to say this is that it exists throughout spacetime and its fluctuations are described by the Klein–Gordon equation. In natural units,

$$\left(\frac{\partial^2}{\partial t^2} + \nabla^2 - m^2 \right) \phi(\vec{x}, t) = 0$$

This equation was the first attempt at a relativistic quantum mechanical equation of a wave. it tells us how the field of a particle fluctuates.

The Klein-Gordon equation can also be written in the Lorentz-invariant form,

$$(\partial^\mu \partial_\mu + m^2) \psi = 0 \quad (6.3)$$

Where,

$$\partial^\mu \partial_\mu u \equiv \frac{\partial^2}{\partial t^2} - \frac{\partial^2}{\partial x^2} - \frac{\partial^2}{\partial y^2} - \frac{\partial^2}{\partial z^2}$$

The Klein-Gordon equation has plane wave solutions,

$$\psi(x, t) = N e^{i(p \cdot x - Et)} \quad (6.4)$$

Substituting in Equation (3),

$$E^2 \psi = p^2 \psi + m^2 \psi$$

Chapter 7

Epilogue: What lies ahead

With all of what we have discussed, whilst being the most experimentally accurate theory, Quantum Mechanics still remains incomplete due to three key issues that arise from internal consistency and consistency with other theories such relativity:

- **Locality:** Why do non-local effects arise in Quantum Mechanics? Are they artifacts of our ignorance or are they real?
- **Measurement:** Why is measurement distinct from time evolution? Why is it stochastic?
- **Ontology:** Is the wavefunction a calculative device or does it actually exist?

This is a realm that might quickly slip into philosophy¹ so we only mention points here and point to reading material since a subject of this depth deserves several volumes to dissect. Various different interpretations and formulations exist in the community that solve one or more of these problems. Few have suggested that Quantum Mechanics is truly deterministic at heart², few more suggest that the measurement problem has a great deal to do with the effect of gravity or some other novel mechanism³, Rovelli suggests that Quantum Mechanics is about how one system is related to another⁴ and a new proposal even goes on to state that classical mechanics is non-deterministic⁵!

¹For a brief overview refer to [27] and [28]

²See [26] and [24]

³See [2]

⁴Read [25]

⁵Read [29]

As exemplified by the diversity of proposals, there is absolutely zero consensus in the community as to which approach is the most fruitful ⁶. Maybe in the future, people will laugh at our ignorance and foolishness. But as form of anaesthesia ⁷, I would quote,

”The aspiration to truth is more precious than its assured possession”

- Gotthold Lessing

⁶See [31]

⁷Or as David Mermim would call it a ”pillow”

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