

# Quantum Mechanics 2 Notes

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# Contents

<b>1</b>	<b>Approximation Methods</b>	<b>4</b>
1.1	Time Independent Perturbation Theory . . . . .	4
1.1.1	Introduction . . . . .	4
1.1.2	Application to Shrodinger's Equation . . . . .	4
1.2	Degenerate Perturbation Theory . . . . .	7
1.2.1	Overview . . . . .	7
1.2.2	Formalism . . . . .	7
1.3	Examples of Perturbation Theory . . . . .	9
1.3.1	Linear Stark Effect . . . . .	9
1.3.2	$\lambda$ Counting . . . . .	10
1.3.3	Spin-Orbit . . . . .	11
1.3.4	Zeeman Effect . . . . .	13
1.3.5	Van der Waals Interaction . . . . .	15
1.4	Variational Method . . . . .	15
1.5	Time-Dependant Perturbation Theory . . . . .	16
1.5.1	Overview . . . . .	16
1.5.2	Formalism . . . . .	16
1.6	Examples of Time Dependent Perturbation Theory . . . . .	18
1.6.1	Constant Perturbation . . . . .	18
1.6.2	Harmonic Perturbation . . . . .	19
1.6.3	Electromagnetic Hamiltonian . . . . .	20
1.6.4	Electric Dipole Approximation . . . . .	21
1.6.5	Photoabsorbption/Photoemission . . . . .	21
1.7	Initial State Decay . . . . .	22
1.7.1	Remarks on Results . . . . .	24
<b>2</b>	<b>Scattering Theory</b>	<b>24</b>
2.1	Formulation . . . . .	24
2.1.1	Particle Beam Scattering . . . . .	25
2.1.2	Overview of Formulation . . . . .	27
2.2	Born Approximation . . . . .	28
2.2.1	Example: Yukawa Potential . . . . .	29
2.2.2	Validity of Born Approximation . . . . .	29
2.3	Partial Wave Expansion . . . . .	30
2.3.1	Formalism . . . . .	30
2.3.2	Infinitely Hard Sphere . . . . .	31
2.3.3	Square Well (Barrier) . . . . .	33
2.3.4	Low Energy Expansions . . . . .	34
2.4	Resonance . . . . .	35
2.4.1	Lifetime . . . . .	36
2.5	High Energy Scattering . . . . .	36
2.5.1	Eikonal Approximation . . . . .	36
2.5.2	High Energy Partial Waves . . . . .	39
2.6	Inelastic Electron-Atom Scattering . . . . .	39
2.6.1	Formulation . . . . .	39

2.6.2	Calculating Interaction Matrix Element . . . . .	40
<b>3</b>	<b>Identical Particles</b>	<b>42</b>
3.1	Formulation . . . . .	42
3.2	Symmetrizing and Anti-symmetrizing . . . . .	42
3.2.1	Two Particles . . . . .	42
3.2.2	Three Particles . . . . .	43
3.3	Fermi Fluid . . . . .	43
3.4	Z Electron Atoms . . . . .	44
3.4.1	Ground States of Atoms . . . . .	44
3.4.2	He Nucleus . . . . .	45
3.4.3	Local Denisty Approximation (Thomas-Fermi) . . . . .	45

# 1 Approximation Methods

This chapter is basically a bunch of tricks about approximations that are useful in Quantum Mechanics. Very often an exact solution is not possible, so we must resort to these methods. We always want to solve a Shrodinger equation such as

$$H|\psi\rangle = E|\psi\rangle. \quad (1.0.1)$$

## 1.1 Time Independent Perturbation Theory

### 1.1.1 Introduction

One method that is very useful is perturbation theory. We can explain this by example. Consider the equation

$$x^2 - 1 = 0, \quad (1.1.1)$$

which can obviously be solved by  $x = \pm 1$ . Now we look at

$$x^2 - 1 = 0.01 \sin x, \quad (1.1.2)$$

which is an equation not solvable analytically. Notice that  $|\sin x| < 1$  and so we can write  $\lambda = 0.01$  and rewrite as

$$x^2 - 1 = \lambda \sin x, \quad (1.1.3)$$

where  $\lambda$  small. So we first solve

$$x_0^2 - 1 = 0, \quad (1.1.4)$$

which implies that  $x_0 = \pm 1$ . Then we substitute this back in and get that

$$x_1^2 - 1 = \lambda \sin x_0 \quad (1.1.5)$$

which implies that

$$x_1 = \pm \sqrt{1 + \lambda \sin x_0}. \quad (1.1.6)$$

If we iterate this process, we get a perturbative series and as  $n \rightarrow \infty$  we get a more exact solution. So the exact solution is a power series in  $\lambda$ . So we get that

$$x = \pm 1 + c_1 \lambda + c_2 \lambda^2 + \dots \quad (1.1.7)$$

This is a fast convergence as long as the perturbation is small enough.

### 1.1.2 Application to Shrodinger's Equation

Often we can separate the Hamiltonian into the form

$$H = H_0 + \lambda V, \quad (1.1.8)$$

where  $|\lambda V| \ll H_0$  and  $H_0$  is known and exactly solvable in the sense

$$H_0 |n^{(0)}\rangle = E_n^{(0)} |n^{(0)}\rangle, \quad (1.1.9)$$

and  $\{|n^{(0)}\rangle\}$ ,  $E_n^{(0)}$  are known. So we have

$$\begin{aligned}
H|n\rangle &= E_n|n\rangle \\
\implies (H_0 + \lambda V)|n\rangle &= E_n|n\rangle = (E_n^{(0)} + \Delta_n)|n\rangle \\
\implies (E_n^{(0)} - H_0)|n\rangle &= (\lambda V - \Delta_n)|n\rangle \\
\implies |n\rangle &= \frac{(\lambda V - \Delta_n)}{E_n^{(0)} - H_0}|n\rangle.
\end{aligned} \tag{1.1.10}$$

This last expression has several problems.

1. How do we divide by operators?
2. The denominator may be zero.
3. We can add an arbitrary constant  $c|n^{(0)}\rangle$ .

So we can fix the third by inserting this constant into the equation

$$|n\rangle = \frac{(\lambda V - \Delta_n)}{E_n^{(0)} - H_0}|n\rangle + c|n^{(0)}\rangle. \tag{1.1.11}$$

To fix the other problems, we can write the state  $|n\rangle = \sum_m \beta_m |m^{(0)}\rangle$ . We note that  $m \neq n$  or else we get a zero. In other words, the right hand side cannot have any component in the  $n^{(0)}$  direction. To show this we can multiply as

$$\langle n^{(0)}|(E_n^{(0)} - H_0)|n\rangle = 0 = \left\langle n^{(0)} \left| \sum_m \beta_m |m^{(0)}\rangle \right. \right\rangle, \tag{1.1.12}$$

so we are not dividing by zero. So we introduce the projection operator

$$\begin{aligned}
\phi_n &= 1 - |n^{(0)}\rangle \langle n^{(0)}| \\
&= \sum_m |m^{(0)}\rangle \langle m^{(0)}| - |n^{(0)}\rangle \langle n^{(0)}| \\
&= \sum_{m \neq n} |m^{(0)}\rangle \langle m^{(0)}|
\end{aligned} \tag{1.1.13}$$

which projects to the orthogonal space to  $|n^{(0)}\rangle$ . So the final equation is

$$|n\rangle = c|n^{(0)}\rangle + \frac{\phi_n}{H_0 - E_n^{(0)}}(\lambda V - \Delta_n)|n\rangle. \tag{1.1.14}$$

Generally, we choose  $c = 1$  which controls the normalization and with that convention we get that

$$\langle n^{(0)}|n\rangle = 1. \tag{1.1.15}$$

Note that the  $\phi_n$  is simply an indication that there is no projection in the  $|n^{(0)}\rangle$  direction. It is a diagonal matrix and commutes with the Hamiltonian. Also note that by choosing  $c = 1$ ,  $\langle n|n\rangle$  is not normalized which is something we need to fix. So now we can write down two perturbation series

$$\begin{cases} \Delta_n &= \lambda \Delta_n^{(1)} + \lambda^2 \Delta_n^{(2)} + \dots \\ |n\rangle &= |n^{(0)}\rangle + \lambda |n^{(1)}\rangle + \lambda^2 |n^{(2)}\rangle + \dots \end{cases} \tag{1.1.16}$$

So we can get that for the lowest order, the energy correction

$$\boxed{\Delta_n^{(1)} = \langle n^{(0)} | V | n^{(0)} \rangle} \quad (1.1.17)$$

which is just the expectation value of the perturbation. Now we can solve for the first order correction to the state as as

$$\begin{aligned} |n^{(1)}\rangle &= \frac{\phi_n}{E_n^{(0)} - H_0} (V - \lambda \langle n^{(0)} | V | n^{(0)} \rangle) |n^{(0)}\rangle \\ &= \frac{\phi_n}{E_n^{(0)} - H_0} (V) |n^{(0)}\rangle \\ &= \sum_{i \neq n} \frac{1}{E_n^{(0)} - H_0} |i^{(0)}\rangle \langle i^{(0)} | V | n^{(0)} \rangle \\ &= \sum_{i \neq n} \frac{V_{in}}{E_n^{(0)} - E_i^{(0)}} |i^{(0)}\rangle. \end{aligned} \quad (1.1.18)$$

since the  $\phi_n$  operating on  $|n^{(0)}\rangle$  will produce zero. And so we get that

$$\boxed{|n^{(1)}\rangle = \sum_{i \neq n} \frac{\langle i^{(0)} | V | n^{(0)} \rangle}{E_n^{(0)} - E_i^{(0)}} |i^{(0)}\rangle} \quad (1.1.19)$$

Now we can find the second order energy correction as

$$\begin{aligned} \Delta_n^{(2)} &= \langle n^{(0)} | V | n^{(1)} \rangle \\ &= \sum_{i \neq n} \frac{V_{ni} V_{in}}{E_n^{(0)} - E_i^{(0)}} \\ &= \sum_{i \neq n} \frac{|V_{in}|^2}{E_n^{(0)} - E_i^{(0)}}, \end{aligned} \quad (1.1.20)$$

and so the second order energy correction is given as

$$\boxed{\Delta_n^{(2)} = \sum_{i \neq n} \frac{|\langle i^{(0)} | V | n^{(0)} \rangle|^2}{E_n^{(0)} - E_i^{(0)}}} \quad (1.1.21)$$

since  $V_{in} = V_{ni}^*$ . The second order energy correction to the ground state is always negative. In general, the second order perturbation produces negative contributions from higher energy states (hence the ground state being pushed down) and positive contributions from lower energy states. To get the correction to the wavefunction, we write

$$\begin{aligned} |n^{(2)}\rangle &= \frac{\phi_n}{E_n^{(0)} - H_0} (\lambda V - \lambda \Delta_n^{(1)}) |n^{(0)}\rangle \\ &= \frac{\phi_n}{E_n^{(0)} - H_0} (V - \langle n^{(0)} | V | n^{(0)} \rangle) \frac{\phi_n}{E_n^{(0)} - H_0} V |n^{(0)}\rangle \\ &= \frac{\phi_n}{E_n^{(0)} - H_0} V \frac{\phi_n}{E_n^{(0)} - H_0} V |n^{(0)}\rangle - V_{nn} \left( \frac{\phi_n}{E_n^{(0)} - H_0} \right)^2 V |n^{(0)}\rangle, \end{aligned} \quad (1.1.22)$$

which we can write as

$$\boxed{|n^{(2)}\rangle = \sum_{i,j \neq n} \frac{V_{ij}V_{jn} |i^{(0)}\rangle}{(E_n^{(0)} - E_i^{(0)})(E_n^{(0)} - E_j^{(0)})} - \sum_{i \neq j} V_{nm} \left( \frac{1}{E_n^{(0)} - E_i^{(0)}} \right)^2 V_{in} |i^{(0)}\rangle} \quad (1.1.23)$$

We can then propagate this further and keep finding corrections. NEED NOTES ON NEUTRAL PARTICLE IN AN ELECTRIC FIELD.

## 1.2 Degenerate Perturbation Theory

### 1.2.1 Overview

So far we have made the assumption that energies are non-degenerate. Our previous formalism would fail because the expression in the denominator of our expressions for the second order energy shift would diverge. One possible way to fix this is to ensure a zero in the numerator, which says the perturbation does not couple degenerate states. Note that the notation here is quite difficult.

We are looking at a  $g$ -dimensional subspace of  $H_0$  which is  $E_0^{(d)}1$ , where 1 is the unit matrix and  $E_0^{(d)}$  is the degenerate energy. So in this subspace, we can start with an arbitrary basis  $\{|m^{(0)}\rangle\}$  of the subspace. We are looking to map this to a basis  $\{|l^{(0)}\rangle\}$  such that in the  $l$  basis, the states are not coupled in the full Hamiltonian. In other words, the interaction is diagonalized. We will write down the  $V$  matrix in the  $\{|m\rangle\}$  basis and diagonalise. This will give us both the basis, zero order energy, and first order energy shift.

### 1.2.2 Formalism

We start with the degenerate space  $P$  (in the book  $P_0$ ), which is the  $g$  dimensional subspace in which the degeneracy occurs.  $Q$  (in the book  $P_1$ ) is the complementary space. Here  $P + Q = 1$ . So imagine that the exact eigenstates are  $\{|l\rangle\}$ . We again want to solve the Schrodinger equation

$$(E - H_0 - \lambda V) |l\rangle = 0. \quad (1.2.1)$$

Since  $P + Q = 1$ , we can transform this equation into

$$(E - H_0 - \lambda V)P |l\rangle + (E - H_0 - \lambda V)Q |l\rangle = 0. \quad (1.2.2)$$

Essentially, we are projecting the Hamiltonian into four blocks

$$H_{proj} = \begin{pmatrix} H_{QQ} & H_{PQ} \\ H_{QP} & H_{PP} \end{pmatrix}. \quad (1.2.3)$$

So first we will calculate the projection into  $P$  space by multiplying by  $P$ .  $P$  commutes with  $H_0$ , but not with  $V$ . So we can write

$$(E - H_0 - \lambda V_{pp})P |l\rangle + -\lambda V_{PQ}Q |l\rangle = 0. \quad (1.2.4)$$

where  $V_{pp} = PVP$ , and  $V_{pq} = PVQ$ . and  $PEQ = 0$  since  $P, Q$  are complementary. We can do the same projection into  $Q$  space which yields

$$-\lambda V_{QP}P |l\rangle + (E - H_0 - \lambda V_{QQ})Q |l\rangle = 0 \quad (1.2.5)$$

So we can solve this  $Q$  space  $|l\rangle$  (the non-degenerate part) by noting that

$$Q |l\rangle = \frac{-\lambda V_{QP} P |l\rangle}{E - H_0 - \lambda V_{QQ}} \quad (1.2.6)$$

So we can also get the equation

$$\left[ E - H_0 - \lambda V_{PP} - \lambda V_{PQ} \frac{1}{E - H_0 - \lambda V_{QQ}} (-\lambda V_{QQ}) \right] P |l\rangle = 0. \quad (1.2.7)$$

We can use this to do perturbation theory. So we arrive at the equation

$$\boxed{[E - H_0 - \lambda V_{PP}] |l^{(0)}\rangle = 0,} \quad (1.2.8)$$

where  $E = E_d + \lambda V_i + \dots$ . So we have the zero order wavefunction and first order energy correction. Now we need the first order wavefunction and second order energy correction. First we will get the first order wavefunction correction. To do this, we will note that

$$|l^{(1)}\rangle = P |l^{(1)}\rangle + Q |l^{(1)}\rangle \quad (1.2.9)$$

First we will look at the  $Q$  part and we get that

$$\begin{aligned} Q |l^{(1)}\rangle &= \frac{1}{E_D^{(0)} - H_0} (-\lambda V_{QP}) P |l\rangle \\ &= \sum_{k \neq g} \frac{1}{E_D^{(0)} - E_k} (-V_{kl}) |k\rangle. \end{aligned} \quad (1.2.10)$$

We can now look at the  $P$  part which is somewhat more complicated. Here we have

$$(E - E_0^{(0)} - \lambda V_{PP}) P |l_i^{(0)}\rangle = 0, \quad (1.2.11)$$

where  $i = 1, 2, \dots, g$  since we are in a  $g$ -dimensional subspace. So the energy eigenvalue which is correspondent to these eigenstates are

$$\boxed{E_l^{(i)} = E_d^{(0)} + \lambda V_i}, \quad (1.2.12)$$

So the first order correction is split by a linear factor of  $\lambda$ . Now we can look at the first wavefunction correction. So we have that

$$|l^{(1)}\rangle = P |l^{(1)}\rangle + Q |l^{(1)}\rangle, \quad (1.2.13)$$

which for the non-degenerate subspace is given by the normal non-degenerate formula

$$Q |l_i^{(1)}\rangle = \sum_{k \notin D} \frac{V_{kl_i} |k\rangle}{E_d^{(0)} - E_k}, \quad (1.2.14)$$

where the summation is over the non-degenerate subspace. Now we can look at the components in the degenerate subspace. We will write

$$P |l_i^{(1)}\rangle = \sum_{j \neq i} \frac{V_{ji}}{E_i^{(1)} - E_j^{(1)}} |l_j^{(0)}\rangle, \quad (1.2.15)$$



applied to the subspace where we have included the first order interaction as

$$V_{ji} = \lambda^2 V_{PQ} \frac{1}{E - H_0 - \lambda V} V_{QP}, \quad (1.2.16)$$

and assumed that the states are no longer degenerate with a new  $H_0$  of

$$H_0 = E - E_d^{(0)} - \lambda V_{PP}. \quad (1.2.17)$$

Also notice that

$$E_i^{(1)} - E_j^{(1)} = (E_0 + \lambda V_i) - (E_0 + \lambda V_j) = \lambda(V_i - V_j). \quad (1.2.18)$$

So we can simplify our expression as

$$\begin{aligned} P |l_i^{(1)}\rangle &= \lambda \sum_{j \neq i} \frac{1}{V_i - V_j} \left\langle l_j^{(0)} | V \frac{Q}{E_d - H_0} V | l_i^{(0)} \right\rangle |l_j^{(0)}\rangle \\ &= \boxed{\lambda \sum_{j \neq i} \sum_{k \notin D} \frac{1}{V_i - V_j} \frac{V_{lj} V_{kl}}{E_d - E_k^{(0)}} |l_j^{(0)}\rangle}. \end{aligned} \quad (1.2.19)$$

Now we can calculate the second order energy correction. We know that

$$\Delta_{li}^{(2)} = \langle l_i^{(0)} | V | l_i^{(1)} \rangle = \langle l_i^{(0)} | VP | l_i^{(1)} \rangle + \langle l_i^{(0)} | VQ | l_i^{(1)} \rangle, \quad (1.2.20)$$

since  $V$  has two pieces, one in the degenerate subspace, and one outside the degenerate subspace. The piece with  $P$  will vanish and so we have that

$$\boxed{\Delta_{li}^{(2)} = \langle l_i^{(0)} | VQ | l_i^{(1)} \rangle = \sum_{k \notin D} \frac{V_{kl} V_{li}}{E_d^{(0)} - E_k^{(0)}}}. \quad (1.2.21)$$

## 1.3 Examples of Perturbation Theory

### 1.3.1 Linear Stark Effect

The hydrogen atom if we ignore spin has degeneracy in all states with  $n > 1$ . So if we look at the  $n = 2$  case, we have the states

$$|n, l, m\rangle = |2, 0, 0\rangle, |2, 1, 1\rangle, |2, 1, -1\rangle, |2, 1, 0\rangle. \quad (1.3.1)$$

If we think of an electric field inducing a perturbation

$$V = -ez|\vec{E}|, \quad (1.3.2)$$

we have a degenerate perturbation theory problem if we assume electrons are “behaved” in the sense that the perturbation does not blow up. We know that  $H_0$  is a unit matrix in this four dimensional subspace. So we can calculate in the order  $|2, 0, 0\rangle, |2, 1, 0\rangle, |2, 1, 1\rangle, |2, 1, -1\rangle$ . Notice that that this only couples states different parity. In addition,  $z$  is a rank one tensor operator, so only states with  $m = 0$  have non-zero elements.

$$V_{PP} = \begin{pmatrix} 0 & \langle 2, 0, 0 | V | 2, 1, 0 \rangle & 0 & 0 \\ \langle 2, 1, 0 | V | 2, 0, 0 \rangle & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}, \quad (1.3.3)$$

which implies that only two energies are changed. These matrix elements can be derived as

$$\boxed{3ea_0|\vec{E}|}. \quad (1.3.4)$$

### 1.3.2 $\lambda$ Counting

Sometimes when we do an expansion as in perturbation theory, we get a nice expansion such as

$$\frac{1}{1+x} = 1 - x + x^2 + \dots, \quad (1.3.5)$$

however, often we have a situation where we want to expand

$$f_1(x)f_2(x)\dots, \quad (1.3.6)$$

which is easy to calculate to first order, but at higher orders it is very hard to keep track of the order. This way of keeping track of the order is called  $\lambda$  counting. However, this is not just “bean-counting” it also has some interesting physics.

Take the Hydrogen atom. We can think of a counting parameter as

$$\alpha = \frac{e^2}{4\pi} \approx \frac{1}{137}, \quad (1.3.7)$$

in natural units where  $\hbar = c = 1$ . In this unit, energy, momentum, 1/distance, and 1/ time all have the same unit. If we assume that the mass of the proton is very heavy, then the only thing we have with any sort of action is the electron moving around. So,

$$E \propto m_e, \quad (1.3.8)$$

since there is nothing else (I will digress here and say this is from a particle physicists point of view). We know that  $m_e c^2 = 511 \text{ keV}/c^2$  in these units and  $E_1 = -13.6 \text{ eV}$ . So there must be a suppression factor. We know there must be a characteristic speed of the electron and we want to make a guess as to the speed in terms of  $c$  the speed of light. The Hydrogen atom is non-relativistic and we make the guess that

$$v_e \approx \alpha c. \quad (1.3.9)$$

It could also be  $\alpha^2$  or  $\alpha^3$ , but it turns out, it is  $\alpha$ . Now we can calculate the kinetic energy as

$$E = \frac{1}{2}mv^2 \sim \alpha^2 m_e \quad (1.3.10)$$

and the momentum is given as

$$p = m\alpha. \quad (1.3.11)$$

Since the system is stable, the potential must be close to the kinetic energy, so the energy  $E_n$  must be proportional to  $\alpha^2$ . So

$$E_n \propto m_e \alpha^2. \quad (1.3.12)$$

We can use  $p$  with the uncertainty relation in these units  $pa_0 \approx 1$ , which gives the Bohr radius as

$$\alpha_0 = \frac{1}{m\alpha}. \quad (1.3.13)$$

Also note that  $1/m$  is the Compton wavelength of the electron, which is the distance scale beneath which quantum field theory is necessary since an electron cannot be localized beneath this distance. Now, we can look at another power of  $\alpha$ ,  $\alpha/m$ . This is the classical radius of the electron. This shows the importance of being able to think in orders of magnitude.

It turns out that the Hydrogen is more complicated than just a Coulomb potential, and one of these corrections is that there are relativistic corrections to the energy

$$\frac{p^2}{2m} \rightarrow \sqrt{p^2 + m^2} - m = \frac{p^2}{2m} - \frac{p^4}{8m^3} + \dots, \quad (1.3.14)$$

where we are in units of  $c = 1$ . So we can do perturbation theory if we want to get a correction to the Bohr energy. We still know it must be proportional to the mass of the electron and some power of  $\alpha$ . We know it should be  $\alpha^4$ , so the correction to the Bohr energy due to relativistic effects is proportional to  $m_e \alpha^4$ . This is a small number (about  $1/10000$ ), so we don't usually worry about it, but we can measure it. We can also calculate this using perturbation theory as

$$\Delta_{nl}^{(1)} = \left\langle n, l, m \left| \left( -\frac{p^4}{8m^3} \right) \right| n, l, m \right\rangle, \quad (1.3.15)$$

where we don't really care about  $m$  quantum number since the momentum to the fourth power is a rank 0 tensor and does not care about orientation. This calculation is done in the book and makes use of many tricks. The result is that

$$\Delta_{nl}^{(1)} = -\frac{1}{2} m^4 \alpha^4 z^4 \left[ -\frac{3}{4n^4} + \frac{1}{n^3(l+1/2)} \right], \quad (1.3.16)$$

which becomes interesting at high  $Z$  and relativistic effects must be taken into account.

### 1.3.3 Spin-Orbit

If we have a proton and an electron which is moving, then the electron is moving in the electric field of the proton which generates a magnetic field since it is a charged particle. This is given as

$$\vec{B} = \frac{\vec{v} \times \vec{E}}{c}, \quad (1.3.17)$$

where  $\vec{E}$  is the electric field of the proton. Since the electron has a magnetic moment given as

$$\vec{\mu} = -g_s \mu_B \vec{S}, \quad (1.3.18)$$

where  $g_s$  is the gyromagnetic ratio which for the electron is about 2 and  $\mu_B$  is the Bohr magneton given as

$$\mu_B = \frac{|e|\hbar}{2m_e c^2}. \quad (1.3.19)$$

So we can write the perturbing Hamiltonian as

$$H' = -\vec{\mu}_e \cdot \vec{B}, \quad (1.3.20)$$

which we can rewrite as

$$H' = g_s \mu_B \frac{\vec{S} \cdot (\vec{v} \times \vec{E})}{c}. \quad (1.3.21)$$

We can write the electric field as

$$\vec{E} = -\frac{1}{e} \nabla V_c(r), \quad (1.3.22)$$

where  $V_c(r)$  is the central potential. So we can write

$$H' = -\frac{g_s \mu_B}{ec} \mu_B \left( \frac{1}{r} \frac{dV_c}{dr} \right) \vec{S} \cdot (\vec{v} \times \vec{r}), \quad (1.3.23)$$

and here we can see the orbital angular momentum come out (with a negative sign and division by the mass) to get that

$$H' = \frac{g_s \mu_B}{ecm} \left( \frac{1}{r} \frac{dV_c}{dr} \right) (\vec{S} \cdot \vec{L}). \quad (1.3.24)$$

This calculation was done in the frame of the electron, not in the frame we are observing and so there is a factor of 2 error since we need to translate the frame. This is not an easy transformation, but it can be found in Jackson as the Thomas precession. So in the correct frame, we arrive at the proper perturbing Hamiltonian as

$$\boxed{H' = \frac{1}{2m^2 c^2} \left( \frac{1}{r} \frac{dV_c}{dr} \right) (\vec{S} \cdot \vec{L})}, \quad (1.3.25)$$

in our normal units. So we want to calculate the first order term as

$$\Delta_{nl}^{(1)} = \langle n, l, m_l, m_s | H' | n, l, m_l, m_s \rangle. \quad (1.3.26)$$

We could use degenerate perturbation theory in this basis and do a ton of work. Or we could switch basis to lift the degeneracy by transforming  $\{L^2, L_z, S^2, S_z\}$  with  $|l, m_l, m_s\rangle$  to  $\{L^2, S^2, J^2, J_z\}$  with  $|n, l, m_j\rangle$  where there is no degeneracy. This is equivalent to diagonalising the subspace in the first basis, which saves us some work. So, we want

$$\begin{aligned} \Delta_{nl}^{(1)} &= \langle nl; m_j | H' | nl; m_j \rangle \\ &= \frac{1}{2m^2 c^2} \left\langle \frac{1}{r} \frac{dV_c}{dr} \right\rangle_{n,l} \langle l; m_j | \vec{L} \cdot \vec{S} | n; m_j \rangle. \end{aligned} \quad (1.3.27)$$

Now using the fact that

$$\vec{L} \cdot \vec{S} = \frac{1}{2} (\vec{J}^2 - \vec{L}^2 - \vec{S}^2), \quad (1.3.28)$$

which is diagonal in our basis and so we use the eigenvalues

$$\langle l; m_j | \vec{L} \cdot \vec{S} | n; m_j \rangle = \frac{1}{2} \left[ j(j+1) - l(l+1) - \frac{1}{2} \left( \frac{1}{2} + 1 \right) \right]. \quad (1.3.29)$$

So we can work through this and get the final result that

$$\boxed{\Delta_{nlj} = -\frac{Z^2 \alpha^2}{2nl(l+1)(l+1/2)} E_B \begin{cases} l & j = l + 1/2 \\ -(l+1) & j = l - 1/2 \end{cases}}, \quad (1.3.30)$$

where  $E_B$  is the Bohr energy. This would predict that the  $S_{1/2}$  and  $P_{1/2}$  states would be the same, however there are higher order effects from QED which produce a Lamb shift and lifts the degeneracy.

### 1.3.4 Zeeman Effect

If we put an atom in an external magnetic field, we can change the canonical momentum

$$\vec{p} \rightarrow \vec{p} - \frac{e\vec{A}}{c}, \quad (1.3.31)$$

where  $\vec{A}$  is the usual vector potential given as  $\nabla \times \vec{A} = \vec{B}$ . However, we can make many gauge transformations on  $\vec{A}$  to get the same  $\vec{B}$ , yet the physics will not change in terms of the physical effects. This leads to a symmetry principle which in practice means we should choose the easiest gauge transformation to deal with in a particular problem. Here, we will choose

$$\vec{A} = \frac{1}{2}\vec{B} \times \vec{r}. \quad (1.3.32)$$

To check that this is a proper vector potential, we note the identity

$$\vec{A} \times (\vec{B} \times \vec{C}) = (\vec{A} \cdot \vec{C})\vec{B} - (\vec{A} \cdot \vec{B})\vec{C}, \quad (1.3.33)$$

which lets us solve

$$\begin{aligned} \vec{B} &= \nabla \times \vec{A} = \frac{1}{2}\nabla \times (\vec{B} \times \vec{r}) \\ &= \frac{1}{2} \left[ \vec{B}(\nabla \cdot \vec{r}) - (\vec{B} \times \nabla)\vec{r} \right] \\ &= \frac{1}{2} \left[ 3\vec{B} - \vec{B} \right] \\ &= \vec{B}, \end{aligned} \quad (1.3.34)$$

which is what we would expect.

$$H = \frac{1}{2m} \left( \vec{p} - \frac{e}{c}\vec{A} \right)^2 + V(r), \quad (1.3.35)$$

which we can rewrite as

$$H = \frac{1}{2m} \left[ \vec{p}^2 - \frac{e}{c} \underbrace{(\vec{p} \cdot \vec{A} + \vec{A} \cdot \vec{p})}_{[\vec{A}, \vec{p}]} + \frac{e^2}{c^2} \vec{A}^2 \right] + V(r), \quad (1.3.36)$$

and if we note that

$$[\vec{A}, \vec{p}] \sim \nabla \cdot \vec{A}, \quad (1.3.37)$$

we can usually rewrite that middle term. This leaves us with the Hamiltonian in the form

$$H = \frac{1}{2m} \left[ \vec{p}^2 - \frac{e}{2c} \left[ (\vec{B} \times \vec{r} \cdot \vec{p} + \vec{p} \cdot (\vec{B} \times \vec{r})) \right] + \frac{e^2}{c^2} \vec{A}^2 \right] + V(r). \quad (1.3.38)$$

Now using the fact that

$$\vec{A} \cdot (\vec{B} \times \vec{C}) = (\vec{A} \times \vec{B}) \cdot \vec{C}, \quad (1.3.39)$$

we can write the Hamiltonian using the definition of  $\vec{L} = \vec{r} \times \vec{p}$  as

$$H = \frac{p^2}{2m} - \frac{e}{2mc} \vec{L} \cdot \vec{B} + \frac{e^2}{2mc^2} \vec{A}^2 + V(r). \quad (1.3.40)$$

However, this is not actually complete since we have not completely included the spin of the electrons. So we can write the Hamiltonian as

$$H = \frac{p^2}{2m} - \frac{e}{2mc}(\vec{L} + 2\vec{S}) \cdot \vec{B} + \frac{e^2}{2mc^2}A^2 + V(r). \quad (1.3.41)$$

If we assume that  $\vec{B} = B_z$  (only in the  $z$  direction), we can write this as a perturbation to the normal Hydrogen atom of

$$V = \frac{-e}{2mc}(L_z + 2S_z)|\vec{B}| + \frac{e^2}{8mc^2}\vec{B}^2(x^2 + y^2). \quad (1.3.42)$$

We also need to add the spin-orbit effect, but we can do this in multiple ways.

$$|\vec{B}| \text{ Internal} \gg |\vec{B}| \text{ External}$$

If  $B_{ext} \ll B_{int}$ , we can ignore the second term which is diamagnetic). We can take as the non-perturbed eigenstates as the eigenstates of the full spin-orbit Hamiltonian in the basis  $|n, l, j, m_j\rangle$ . So now we can calculate the energy shift as

$$\Delta_{n,l,j,m_j}^{(1)} = \left\langle n, l, j, m_j \left| \left( -\frac{e}{2mc} \right) (L_z + S_z) \right| n, l, j, m_j \right\rangle B_z. \quad (1.3.43)$$

The simplest way to calculate this is to write it as some kind of scalar product, which is shown in the textbook. So we can write the energy shift ( $\Delta E_B$  in textbook) as

$$\Delta_{n,l,j,m_j}^{(1)} = \frac{-e\hbar B}{2m_e c} m_j \left[ 1 \pm \frac{1}{2l+1} \right], \quad (1.3.44)$$

where the  $\pm$  depends on  $j$ .

$$|\vec{B}| \text{ External} \gg |\vec{B}| \text{ Internal}$$

This is called the Paschen-Back limit. Here we also ignore the diamagnetic term, but we treat the non-perturbed Hamiltonian without the spin-orbit interaction, and then add the spin-orbit term in as a small perturbation after. So now we work in the basis

$$[L^2, L_z, S^2, S_z] \rightarrow |l, m_l, s, m_s\rangle, \quad (1.3.45)$$

So we have that

$$\begin{aligned} \Delta_{l,m_l,s,m_s}^{(1)} &= \frac{-e}{2mc} \langle l, m_l, s, m_s | (L_z + 2S_z) | l, m_l, s, m_s \rangle \\ &= \left[ \frac{-e}{2mc} (m_l + 2m_s) \right]. \end{aligned} \quad (1.3.46)$$

Now we evaluate the spin-orbit interaction in this basis as

$$\begin{aligned} \langle \vec{L} \cdot \vec{S} \rangle &= \left\langle L_z S_z + \frac{1}{2}(L_+ S_- + L_- S_+) \right\rangle \\ &= \langle L_z S_z \rangle \\ &= m_l m_s, \end{aligned} \quad (1.3.47)$$

which implies that

$$V_{SO} = \frac{m_l m_s \hbar^2}{2m_e^2 c^2} \left\langle \frac{1}{r} \frac{dV}{dr} \right\rangle. \quad (1.3.48)$$

### 1.3.5 Van der Waals Interaction

Two atoms that are separated will induce dipole moments in each other as there is a fluctuating dipole moment due to fluctuations in each individual atom. This produces a potential of the form

$$V(r) = -\frac{a}{r^6}. \quad (1.3.49)$$

So if we have atom 1 and atom 2 with distance between them  $r$ . The first atom has an electron at radius  $r_1$  and the second has an electron at radius  $r_2$ . So we can write down the Hamiltonian

$$H = \frac{p_1^2}{2m_1} + V(\vec{r}_1) + \frac{p_2^2}{2m_2} + V(\vec{r}_2) + V_{int}, \quad (1.3.50)$$

where  $V_{int}$  is the interaction between the two systems and can be written as a sum of nuclear and electronic repulsions and attractions. which gives

$$V_{int} = \frac{e^2}{r} + \frac{e^2}{|\vec{r} + \vec{r}_1 + \vec{r}_2|} - \frac{e^2}{|\vec{r} + \vec{r}_2|} - \frac{e^2}{|\vec{r} + \vec{r}_1|}. \quad (1.3.51)$$

When the atoms are far apart, we can expand in a Taylor series and calculate which leaves us with the perturbation

$$V_{int} = \frac{e^2}{r^3} [\vec{r} \cdot \vec{p}_1 \cdot \vec{p}_2 - 3(\vec{p}_1 \cdot \hat{r})(\vec{p}_2 \cdot \hat{r})]. \quad (1.3.52)$$

So we can calculate this as the expectation value of the wavefunction

$$\Delta^{(1)} = \langle \psi_{100} \psi_{100} | V_{int} | \psi_{100} \psi_{100} \rangle = 0, \quad (1.3.53)$$

since these wavefunctions are spherically symmetric. There is no dipole moment expectation value for spherical symmetry. So we must go to second order in order to calculate this. So we have that

$$\Delta^{(2)} = \sum_{k \neq 0} \frac{|\langle k | V_{int} | 0 \rangle|^2}{E_0 - E_k}. \quad (1.3.54)$$

We can already say two things about this without calculating this. We are going to get a negative number and it is going to go as  $1/r^6$  since we are squaring a  $1/r^3$  term.

## 1.4 Variational Method

This is a non-perturbative method. The idea is that we have a Hamiltonian  $H$ , which we have no idea how to solve. If we guess a wavefunction  $\psi_g$  (where  $g$  for guess), then

$$E_g = \langle \psi_g | H | \psi_g \rangle \geq E_0. \quad (1.4.1)$$

This is because we can expand our guess wavefunction in terms of the actual wavefunction  $\psi$  as

$$|\psi_g\rangle = \sum_{n=0}^{\infty} c_n |\psi_n\rangle, \quad (1.4.2)$$

which implies that

$$\begin{aligned}
E_g &= \langle \psi_g | H | \psi_g \rangle \\
&= \sum_{n,m} \underbrace{\langle m | H | n \rangle}_{\delta_{m,n}} c_n c_m^* \\
&= \sum_{n=0}^{\infty} |c_n|^2 E_n \\
&\geq \sum_{n=0}^{\infty} E_0 |c_n|^2 \\
&= E_0,
\end{aligned} \tag{1.4.3}$$

which implies that

$$\boxed{\langle \psi_g | H | \psi_g \rangle \geq E_0}. \tag{1.4.4}$$

This is useful because we can make a test wavefunction depend on many parameters  $\psi_g(\lambda_1, \lambda_2, \dots)$  and get a guess  $E_g(\lambda_1, \dots)$ , then we can minimize  $E_g$  with respect to all parameters. So the real work is to guess the closest wavefunction.

## 1.5 Time-Dependant Perturbation Theory

### 1.5.1 Overview

This is the case where the Hamiltonian evolves in time and we want to approximate the time dependent Schrodinger equation. Here we will have only the perturbation (or interaction) part evolve in time. Suppose that we have a Hamiltonian as a function of time

$$H(t) = H_0 + V(t), \tag{1.5.1}$$

and we want to solve the Schrodinger equation

$$i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle = H(t) |\psi(t)\rangle. \tag{1.5.2}$$

So if we have eigenstates of the  $H_0$

$$H_0 |n^{(0)}\rangle = E_n^{(0)} |n^{(0)}\rangle, \tag{1.5.3}$$

we want to know the probability of them in a some state as a function of time  $p_n(t)$ .

### 1.5.2 Formalism

To solve the problem give above we will introduce the interaction picture, otherwise known as the Dirac Picture. We have previously seen the Schrodinger picture (state evolves in time, operators do not), the Heisenberg picture (operators evolve in time, states are stationary).

The Dirac picture is somewhere in between. The operator evolution and the state evolution are controlled by the two parts of the Hamiltonian. So the state is the Schrodinger picture state

$$|\psi\rangle_I = e^{iH_0 t/\hbar} |\psi\rangle_S \tag{1.5.4}$$



and the operator is

$$O_I = e^{iH_0t/\hbar} O_S e^{-iH_0t/\hbar}, \quad (1.5.5)$$

where the subscripts  $S, I, H$  label the different pictures. So we know that the operator evolution is controlled completely by  $H_0$  and given as

$$i\hbar \frac{\partial}{\partial t} O_I(t) = [O_I(t), H_0]. \quad (1.5.6)$$

Looking at the Schrodinger equation for the state, we see that

$$\begin{aligned} i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle_I &= -H_0 |\psi\rangle_S + e^{iH_0t/\hbar} \left( i\hbar \frac{\partial}{\partial t} |\psi\rangle_S \right) (H_0 + V(t)) |\psi\rangle_S \\ &= e^{iH_0t/\hbar} V(t) e^{-iH_0t/\hbar} |\psi\rangle_I \\ &= V_I(t) |\psi\rangle_I. \end{aligned} \quad (1.5.7)$$

Thus in the interaction picture, the interactions control the state evolution and the operators are controlled by the  $H_0$ .

Now we need to think about our original problem in the interaction picture. So we can write

$$|\psi\rangle_I(t) = \sum_n c_n(t) |n\rangle, \quad (1.5.8)$$

so it is just the coefficient which is evolving in time. We can also write this in terms of a matrix. So we can write

$$i\hbar \frac{\partial}{\partial t} \begin{pmatrix} c_1(t) \\ c_2(t) \\ \vdots \end{pmatrix} = (V_I)_{nm} \begin{pmatrix} c_1(t) \\ c_2(t) \\ \vdots \end{pmatrix} \quad (1.5.9)$$

Where

$$\begin{aligned} (V_I)_{nm} &= \langle n | e^{iH_0t/\hbar} V(t) e^{-iH_0t/\hbar} | m \rangle \\ &= e^{i(E-n-E_m)t/\hbar} \langle m | V(t) | n \rangle. \end{aligned} \quad (1.5.10)$$

So if we define

$$V_{nm}(t) = \langle m | V(t) | n \rangle \quad (1.5.11)$$

$$\omega_{nm} = \frac{E_n - E_m}{\hbar}, \quad (1.5.12)$$

we can write

$$i\hbar \frac{\partial}{\partial t} \begin{pmatrix} c_1(t) \\ c_2(t) \\ \vdots \end{pmatrix} = \begin{pmatrix} V_{11}(t) & V_{12}e^{i\omega_{12}t} & \dots \\ V_{21}e^{i\omega_{21}t} & V_{22} & \dots \\ \vdots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} c_1(t) \\ c_2(t) \\ \vdots \end{pmatrix}. \quad (1.5.13)$$

In the  $2 \times 2$  place where

$$H_0 = \begin{pmatrix} E_1 & 0 \\ 0 & E_2 \end{pmatrix} \quad (1.5.14)$$

Then we know that

$$V(t) = \begin{pmatrix} 0 & \gamma e^{i\omega t} \\ \gamma e^{-i\omega t} & 0 \end{pmatrix}, \quad (1.5.15)$$

where  $\gamma$  is real, although this will not matter in the end since we can change the basis to get rid of the phase the complex  $\gamma$  would induce. We want to write this down in the interaction picture. So we will have

$$i\hbar \frac{\partial}{\partial t} \begin{pmatrix} c_1(t) \\ c_2(t) \end{pmatrix} = \begin{pmatrix} 0 & \gamma e^{i\omega t + i\omega_{12}t} \\ \gamma e^{-i\omega t + \omega_{21}t} & 0 \end{pmatrix} \begin{pmatrix} c_1(t) \\ c_2(t) \end{pmatrix}. \quad (1.5.16)$$

We will solve this in homework, but we will get the answer here. If we start where  $c_1(0) = 1$ , and  $c_2(0) = 0$ , then we have the Rabi formula

$$P_2(t) = |c_2(t)|^2 = \frac{\gamma^2}{(\Omega\hbar)^2} \sin^2(\Omega t), \quad (1.5.17)$$

where  $\Omega$  is the Rabi frequency given by

$$\Omega = \sqrt{\frac{\gamma^2}{\hbar^2} + \frac{(\omega - \omega_{21})^2}{4}}. \quad (1.5.18)$$

Note here we have implicitly assumed without loss of generality that  $E_2 < E_1$  and so note that  $\omega_{21} = -\omega_{12}$ .

Back to the general case. We have a set of matrix equations, so we can solve each independently as

$$i\hbar \frac{\partial}{\partial t} c_n^{(1)} = V_{ni}(t) e^{i\omega_{ni}t} c_i^{(0)} \quad (1.5.19)$$

which implies that

$$c_n^{(1)} = -\frac{i}{\hbar} \int_0^t dt e^{\omega_{ni}t} V_{ni}(t), \quad (1.5.20)$$

where  $c_i^{(0)} = 1$ . for the moment, we are not considering  $n = i$ . Now to do the second order perturbation, we can write

$$i\hbar \frac{\partial}{\partial t} c_n^{(2)} = \sum_m V_{nm}(t) e^{i\omega_{nm}t} c_m^{(1)}(t), \quad (1.5.21)$$

which we can write as

$$c_n^{(2)} = \left(\frac{-i}{\hbar}\right)^2 \sum_m \int_0^t dt' V_{nm}(t') e^{i\omega_{nm}t'} \int_0^{t'} dt'' e^{i\omega_{mi}t''} V_{mi}(t''). \quad (1.5.22)$$

Higher order series can be written in the exact same way with more sums and integrals.

## 1.6 Examples of Time Dependent Perturbation Theory

### 1.6.1 Constant Perturbation

Lets start with the simplest constant potential and no degenerate states

$$V(t) = \begin{cases} 0 & t < 0 \\ V & t \geq 0 \end{cases} \quad (1.6.1)$$

So we can find the first order shift as

$$\begin{aligned}
c_n^{(1)} &= -\frac{i}{\hbar} \int_0^t dt' e^{i\omega_{ni}t'} V_{ni} \\
&= -\frac{i}{\hbar} V_{ni} \left[ \frac{1}{i\omega_{ni}} (e^{i\omega_{ni}t} - 1) \right] \\
&= -\frac{1}{\omega_{ni}\hbar} V_{ni} (e^{i\omega_{ni}t} - 1).
\end{aligned} \tag{1.6.2}$$

So this implies that

$$p_{i \rightarrow n}(t) = 4 \frac{|V_{ni}|^2}{(\hbar\omega_{ni})^2} \sin^2 \left( \frac{\omega_{ni}t}{2} \right) \tag{1.6.3}$$

We can work out an argument that says that the probability of long times increases. Here at long  $t$ , our probability goes to

$$P_{i \rightarrow n}(t) \left( \frac{2\pi}{\hbar} \right) |V_{ni}|^2 \delta(E_n - E_i) t, \tag{1.6.4}$$

so we can also calculate the transition rate

$$\boxed{\omega_{i \rightarrow n} = \frac{dP_{i \rightarrow n}(t)}{dt} = \left( \frac{2\pi}{\hbar} \right) |V_{ni}|^2 \delta(E_n - E_i)}, \tag{1.6.5}$$

so at long times only states with same energies can have transitions. However, at not long times, we can have transitions. This is called the Fermi Golden rule.

### 1.6.2 Harmonic Perturbation

Now we will examine the Harmonic perturbation where

$$V_{ni}(t) = v_{ni} e^{i\omega t} + (v^\dagger)_{ni} e^{-i\omega t}. \tag{1.6.6}$$

We will have

$$c_n^{(1)}(t) = -\frac{i}{\hbar} \int_0^t (v_{ni} e^{i\omega t} + (v^\dagger)_{ni} e^{-i\omega t}) e^{i\omega_{ni}t} dt. \tag{1.6.7}$$

We will not work through the rest of this problem, but it is done in the textbook. The basic result is that the first term gives

$$\boxed{E_i = E_n + \hbar\omega}, \tag{1.6.8}$$

which is the energy quanta of the perturbation. This is called a stimulated emission. The probability is given as

$$\omega_{i \rightarrow n} = \frac{2\pi}{\hbar} |v_{ni}|^2 \delta(E_i - E_n - \hbar\omega), \tag{1.6.9}$$

the Fermi-Golden rule for this problem. The other term gives

$$\boxed{E_n - E_i = \hbar\omega}, \tag{1.6.10}$$

which is known as absorption. We can write the transition rate Fermi Golden rule as

$$\omega_{i \rightarrow n} = \frac{2\pi}{\hbar} |(v^\dagger)_{ni}|^2 \delta(E_n - E_i - \hbar\omega), \tag{1.6.11}$$

and we note that both must occur to conserve energy. Note that the if we want to talk about transitions, we also must consider the density of states. This allows us to derive for a two state system

$$\boxed{\frac{1}{\rho(E_1)} \sum \omega_{2 \rightarrow 1} = \frac{1}{\rho(E_2)} \sum \omega_{1 \rightarrow 2}}, \quad (1.6.12)$$

where  $\rho$  is the density of states. This called the detailed balance principle. This arises from the Hermiticity of the interaction. However, it is only true to first order in perturbation theory. It breaks down when there is a system which breaks time reversal invariance.

### 1.6.3 Electromagnetic Hamiltonian

We have a proton with an electron which has an incident plane wave in the  $\hat{n}$  direction. Let  $\hat{\epsilon}$  be perpendicular to  $\hat{n}$ . We can choose a gauge and here we will choose

$$\vec{A} = 2A_0\hat{\epsilon} \cos(\vec{k} \cdot \vec{r} - \omega t). \quad (1.6.13)$$

which will give us  $\vec{E}$  and  $\vec{B}$  as

$$\begin{cases} \vec{E} = -\frac{1}{c} \frac{\partial \vec{A}}{\partial t} \\ \vec{B} = \nabla \times \vec{A} \end{cases} \quad (1.6.14)$$

So in this case, we have that

$$\vec{E} = -\frac{2\omega}{c} A_0 \hat{\epsilon} \sin(\vec{k} \cdot \vec{r} - \omega t), \quad (1.6.15)$$

and

$$\begin{aligned} \vec{B} &= -2A_0(\nabla \vec{k} \cdot \vec{r}) \times \hat{\epsilon} \sin(\vec{k} \cdot \vec{r} - \omega t) \\ &= -2A_0(\vec{k} \times \hat{\epsilon}) \sin(\vec{k} \cdot \vec{r} - \omega t) \end{aligned} \quad (1.6.16)$$

So now we use the Hamiltonian

$$H = \frac{1}{2m} \left( p - \frac{e}{c} \vec{A} \right)^2 - V_c(r). \quad (1.6.17)$$

which we can write as

$$\frac{p^2}{2m} - \frac{e}{mc} \vec{p} \cdot \vec{A} + \frac{1}{2m} \left( \frac{e}{c} \vec{A} \right)^2 + V_c(r), \quad (1.6.18)$$

Which we can write as  $H = H_0 + H'$  where

$$H' = \frac{-e}{mc} \vec{p} \cdot \vec{A} = -\frac{e}{mc} A_0 (\vec{p} \cdot \hat{\epsilon}) \left( e^{i(\vec{k} \cdot \vec{r} - \omega t)} + e^{-i(\vec{k} \cdot \vec{r} - \omega t)} \right), \quad (1.6.19)$$

where we have expanded the cos term in terms of complex exponential. We can rewrite this as

$$V e^{i\omega t} + V^\dagger e^{-i\omega t}, \quad (1.6.20)$$

where

$$V^\dagger = -\frac{e}{mc} A_0 (\vec{p} \cdot \hat{\epsilon}) e^{i\vec{k} \cdot \vec{r}}, \quad (1.6.21)$$

and  $\omega = c|\vec{k}|$ . Now we want to write down the Fermi Golden rule for this system. For absorption (second term), we can write this as

$$\begin{aligned}\omega_{i \rightarrow n} &= \frac{2\pi}{\hbar} |\langle n | V^\dagger | i \rangle|^2 \delta(E_n - E_i - \hbar\omega) \\ &= \boxed{\frac{2\pi e^2}{\hbar m^2 c^2} A_0^2 \left| \langle n | \vec{p} \cdot \vec{\epsilon} e^{i\vec{k} \cdot \vec{r}} | i \rangle \right|^2 \delta(E_n - E_i - \hbar\omega)}\end{aligned}\quad (1.6.22)$$

Very often we will use a concept called absorption cross section which is the ratio between the energy absorbed per time, which is the transition probability times the energy, and flux which is the amount passing through per unit time per unit area. So we can write

$$\sigma = \frac{\omega_{i \rightarrow n} \cdot \hbar\omega}{I}, \quad (1.6.23)$$

where we notice that the flux is just the intensity and this quantity has units of area. For a light source, we can find the intensity as  $I = Uc$ , where  $U$  is energy density and  $c$  is the speed of light at which it is moving. So this is given as

$$\sigma = \frac{1}{2\pi} \frac{\omega^2}{c} |A_0|^2 \quad (1.6.24)$$

#### 1.6.4 Electric Dipole Approximation

The electric dipole approximation is when we write

$$\boxed{e^{i(\omega/c)\vec{n} \cdot \vec{x}} = 1 + i\frac{\omega}{c}\vec{n} \cdot \vec{x} + \dots} \quad (1.6.25)$$

the normal Taylor series, and we keep on the first term 1. This is saying that the wavelength of the radiation field is much longer than the atomic dimension.

#### 1.6.5 Photoabsorbtion/Photoemission

First we remember that

$$\sigma_{ab} = \frac{4\pi^2 \alpha_{em} \hbar}{m_e^2 \omega} \left| \langle n | \vec{\epsilon} \cdot \vec{p} e^{i\vec{q} \cdot \vec{x}} | i \rangle \right|^2 \delta(E_f - E_i - \hbar\omega), \quad (1.6.26)$$

where  $\omega$  is the frequency of the photon being absorbed or emmited and  $\vec{q}$  is on order  $1/\lambda$  and  $\vec{x}$  is on order of the bohr radius. So we have that

$$\vec{x} \cdot \vec{q} \sim \frac{a_0}{\lambda} \ll 1, \quad (1.6.27)$$

so we can neglect this term by taking only the first term in the Taylor expansion. This is another statement of the dipole approximation. We will deviate from the textbook calculation. So we will say that we are looking at a transition from  $\vec{k}_i \rightarrow \vec{k}_f$ . So we can write the number of states as

$$\int \frac{d^3x d^3p}{h^3} \sim V \frac{d^3\vec{k}_f \hbar^3}{h^3} \sim \frac{V}{(2\pi)^3} d^3\vec{k}_f \quad (1.6.28)$$

which implies that we can write

$$d\sigma_{ab} = \frac{4\pi^2\alpha_{em}\hbar}{m_e^2\omega} \left| \int e^{-i\vec{k}_f \cdot \vec{x}} e^{i\vec{q} \cdot \vec{x}} \vec{\epsilon} \cdot \vec{p} \psi_i(\vec{x}) \right|^2 \delta(E_f - E_i - \hbar\omega) \frac{V}{(2\pi)^2} d^3\vec{k}_f \quad (1.6.29)$$

now using the fact that

$$d^3\vec{k}_f = d\Omega_f k_f^2 dK_f \quad (1.6.30)$$

and the fact that  $E_f = \hbar^2 k_f^2 / (2m)$ , we can manipulate the equation and integrate over the delta function to get that

$$d\sigma_{ab} = \frac{k_f \alpha_{em} \Omega_f}{m_e \omega \hbar} \left| \int e^{-i\vec{k}_f \cdot \vec{x}} e^{i\vec{q} \cdot \vec{x}} \vec{\epsilon} \cdot \vec{p} \psi_i(\vec{x}) \right|^2 \quad (1.6.31)$$

Now we can use the energy conservation as  $E_f = E_i + \hbar\omega$  and the momentum conservation, which says that

$$\int e^{-i\vec{k}_f \cdot \vec{x}} e^{i\vec{q} \cdot \vec{x}} \vec{\epsilon} \cdot \vec{p} \psi_i(\vec{x}) = (\vec{\epsilon} \cdot \vec{k}_i) \int e^{-i\vec{k}_i \cdot \vec{x}} \psi_i(x) d^3\vec{x}, \quad (1.6.32)$$

and we can notice the integral is just the Fourier transform of the initial wavefunction in momentum space. So this implies that

$$d\sigma_{ab} = \frac{k_f \alpha_{em} \Omega_f}{m_e \omega \hbar} (\vec{\epsilon} \cdot \vec{k}_i)^2 |\psi_i(k_i)|^2. \quad (1.6.33)$$

## 1.7 Initial State Decay

We have a nice result (Fermi Golden rule) about how a state  $|i\rangle \rightarrow |n\rangle$  decays in terms of a rate. However if  $i \neq n$ , we have a special case and we need some different tools. So if we start in state  $|i\rangle$ , then  $c_i(0) = 1$  and the probability we want is  $|c_i(t)|^2$ . So we can write

$$c_i(t) = c_i^{(0)} + c_i^{(1)} + c_i^{(2)} + \dots, \quad (1.7.1)$$

and we will use the adiabatic approach since the normal perturbation theory will fail. So here we assume that instead of the perturbation being suddenly turned on at  $t = 0$ , we will assume it is gradually ramped from  $t = -\infty \rightarrow 0$ , reaching its final value there. So we assume the perturbation for  $t < 0$  is of the form

$$V e^{\eta t}, \quad (1.7.2)$$

where  $\eta$  is very small and positive. At the end of the calculation, we will let  $\eta \rightarrow 0$ . So now we can write the first order term as

$$\begin{aligned} c_i^{(1)} &= -\frac{i}{\hbar} \int_{-\infty}^t V_{ii}(t) e^{i\omega_{11}t} dt \\ &= -\frac{i}{\hbar} \int_{-\infty}^t V_{ii} e^{\eta t} dt \\ &= \frac{-i}{\hbar} \left( \frac{1}{\eta} \right) e^{\eta t} V_{ii}, \end{aligned} \quad (1.7.3)$$

Note we have not taken  $\eta \rightarrow 0$  yet. This is why this is not extremely rigorous mathematically. We can also calculate higher order terms in the same matter. These terms will go as  $1/\eta^\alpha$ , where  $\alpha$  is the order of the term in the perturbation theory. Now notice that

$$\frac{dc_i}{dt} = 0 - \frac{i}{\hbar} e^{\eta t} V_{ii}, \quad (1.7.4)$$

and we see that the problematic  $\eta$  in the denominator has been canceled. This is not quite the same for higher order terms. If we write the full series, we get that

$$\frac{dc_i(t)}{dt} = -\frac{i}{\hbar} \underbrace{\left( V_{ii} + \sum_m \frac{V_{im}V_{im}}{E_i - E_m + i\eta\hbar} + \dots \right)}_{\Delta_{ii}} c_i(t) \quad (1.7.5)$$

and so we can write

$$\frac{dc_i(t)}{dt} = -\frac{i}{\hbar} \Delta_{ii} c_i(t), \quad (1.7.6)$$

which we can solve as

$$\boxed{c_i(t) = c_i(0)e^{-i\Delta_{ii}t/\hbar}}, \quad (1.7.7)$$

which is very odd because it would seem the probability  $|c_i(t)|^2 = 1$ , however,  $\Delta_{ii}$  has a complex part in the denominator, so  $\Delta_{ii}$  is complex. Now we will use the fact that

$$\frac{1}{x + i\epsilon} = P\left(\frac{1}{x}\right) - i\pi\delta(x), \quad (1.7.8)$$

where  $P(x)$  is the principal value. So we can write

$$\Delta_{ii} = \text{Re}(\Delta_{ii} + i\text{Im}(\Delta_{ii})), \quad (1.7.9)$$

where

$$\text{Im}(\Delta_{ii}) = -\pi \sum_m |V_{im}|^2 \delta(E_i - E_m). \quad (1.7.10)$$

So now we can plug this into our equation as

$$c_i(t) = c_i(0)e^{-i\text{Re}(\Delta_{ii})t + \text{Im}(\Delta_{ii})t}, \quad (1.7.11)$$

which implies that

$$P_i(t) = |c_i(t)|^2 = |c_i(0)|^2 e^{2\text{Im}(\Delta_{ii})t} \quad (1.7.12)$$

So now plugging in our expression for  $\text{Im}(\Delta_{ii})$  and taking a derivative we get that

$$\boxed{\frac{dP_i}{dt} = -\frac{2\pi}{\hbar} \sum_m |V_{im}|^2 \delta(E_i - E_m)}, \quad (1.7.13)$$

which is a sum of Fermi golden rules for all the other states. This is how probability is conserved. If we let

$$\omega_{i \rightarrow m} = \frac{dP_i}{dt} = \frac{\Gamma_i}{\hbar}, \quad (1.7.14)$$

then we have defined the decay width. If one tries to verify (5.9.20) to verify the unitary condition, one needs to normalize  $c_i(t)$  by dividing by  $\sqrt{|c_i(0)|^2}$  or it will not work. If we define  $\tau = \hbar/\Gamma_i$  then we can see that

$$|c_i|^2 = e^{-t/\tau}, \quad (1.7.15)$$

we can see that  $\tau$  is the lifetime of its state, where  $\tau$ , the state has decayed to  $1/e$  of its probability. Now to see why we call  $\Gamma_i$  the decay width, look at the Fourier transform

$$\begin{aligned} f(E) &= \int dt e^{iE_i/\hbar} c_i(t) \\ &= \int_0^\infty dt e^{iEt/\hbar} e^{-i(E_i + \Delta E_i)/\hbar - \Gamma_i t/(2\hbar)} \\ &= -\frac{1}{(E - E'_i)/\hbar - \Gamma_i/2\hbar}, \end{aligned} \quad (1.7.16)$$

where  $E'_i = E_i + \Delta E_i$ . So we can see that

$$|f(E)|^2 = \frac{\hbar^2}{(E - E_i)^2 + \frac{\Gamma_i^2}{4}}, \quad (1.7.17)$$

which is a Lorentzian, where  $\Gamma_i$  can be identified as the full width at half maximum. Notice that

$$\lim_{\Gamma_i \rightarrow 0} |f(E)|^2 = \frac{\pi}{\hbar} \delta(E_i - E_m). \quad (1.7.18)$$

Also notice that  $\Delta E \Delta T \sim \hbar$ , which is the uncertainty relation.

### 1.7.1 Remarks on Results

1. If we wish to calculate the harmonic perturbation, then

$$E_m - E_i \rightarrow E_m - E_i \pm \hbar\omega. \quad (1.7.19)$$

2. For the ground state  $\Gamma_i = 0$  since there is no lower energy. We can see this by noting that

$$\Gamma_i \propto -\pi \sum_{m \neq i} |V_{im}|^2 \delta(E_i - E_m), \quad (1.7.20)$$

which is zero since there is in general no degeneracy in the ground state (with few exceptions).

3. The excited states, can either transition or interact with the vacuum.

In general, since the energy shift for this state has an imaginary part, it has a decay width.

## 2 Scattering Theory

### 2.1 Formulation

The general problem is that we have a particle or a group of particles being exposed to a potential at some time and we want to look at the transition to a continuum final state. We can look at this as a single particle and use time dependant perturbation theory with the adiabatic approximation, or as a beam of particles and use time- independent perturbation theory. The general problem is shown in Figure 1



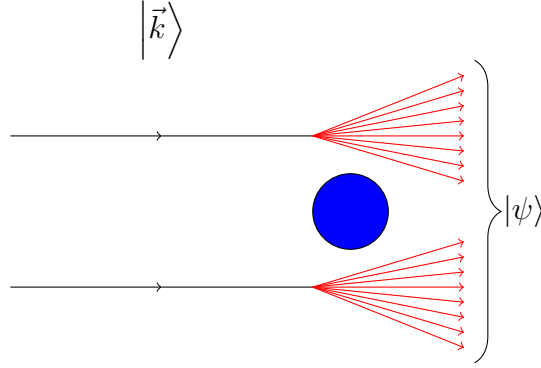


Figure 1: General scattering theory problem from initial state  $|\vec{k}\rangle$  to  $|\psi\rangle$

### 2.1.1 Particle Beam Scattering

So in this case we have a particle beam with constant flux, and we want to solve the Schrodinger equation

$$(H_0 + V) |\psi\rangle = E |\psi\rangle, \quad (2.1.1)$$

where

$$E = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m}, \quad (2.1.2)$$

and  $k = p/\hbar$ . If we re-arrange this, we get

$$(E - H_0) |\psi\rangle = V |\psi\rangle. \quad (2.1.3)$$

This is a second order homogeneous differential equation. We solve this in steps.

1. Find the general solution to the homogeneous equation,

$$(E - H_0) |\phi\rangle = \phi, \quad (2.1.4)$$

which is solved by  $|\phi\rangle = |\vec{k}\rangle$ , where  $|\vec{k}| = k$ .

2. Find the particular solution. We can write the equation as

$$|\psi\rangle = \underbrace{\frac{1}{E - H_0}}_{\text{Green's function}} V |\psi\rangle \quad (2.1.5)$$

To avoid the singularity, we can write

$$|\psi^\pm\rangle = \frac{1}{E - H_0 \pm i\epsilon} V |\psi^\pm\rangle, \quad (2.1.6)$$

where  $\epsilon > 0$ .

3. Now we need to match the boundary condition. We can write down the Lippman-Schwinger Equation which is the general solution plus the particular solution

$$|\psi^\pm\rangle = |\vec{k}\rangle + \frac{1}{E - H_0 \pm i\epsilon} V |\psi^\pm\rangle, \quad (2.1.7)$$

Now we can normalize this function and look at

$$\langle x|\psi^\pm\rangle = \langle x|\vec{k}\rangle + \left\langle x\left|\frac{1}{E-H_0\pm i\epsilon}V\right|\psi^\pm\right\rangle, \quad (2.1.8)$$

and noting that  $\langle \vec{k}'|\vec{k}\rangle = \delta(\vec{k}-\vec{k}')$ , then we have this is equivalent to

$$\frac{e^{i\vec{k}\cdot\vec{x}}}{(2\pi)^{3/2}} + \int d^3x' \left\langle x\left|\frac{1}{E-H_0\pm i\epsilon}\right|x'\right\rangle \langle x'|V|\psi^\pm\rangle, \quad (2.1.9)$$

and then we have a Green's function

$$G_{pm}(x, x') = \frac{\hbar^2}{2m} \left\langle x\left|\frac{1}{E-H_0\pm i\epsilon}\right|x'\right\rangle \quad (2.1.10)$$

We now must switch to a momentum basis, where this is diagonalized, so we can write

$$\begin{aligned} G_\pm(x, x') &= \frac{\hbar^2}{2m} \int d^3k' d^3k'' \langle x|\vec{k}'\rangle \left\langle \vec{k}'\left|\frac{1}{E-H_0\pm i\epsilon}\right|\vec{k}''\right\rangle \langle \vec{k}''|x'\rangle \\ &= \frac{\hbar^2}{2m} \int d^3k' d^3k'' \frac{e^{i\vec{k}'\cdot\vec{x}}}{(2\pi)^{3/2}} \left\langle \vec{k}'\left|\frac{1}{\frac{\hbar^2}{2m} - \frac{\hbar^2(k'')^2}{2m} \pm i\epsilon}\right|\vec{k}''\right\rangle \frac{e^{i\vec{k}''\cdot\vec{x}'}}{(2\pi)^{3/2}} \\ &= \int d^3k' \left( \frac{e^{i\vec{k}'\cdot(\vec{x}-\vec{x}')}}{(2\pi)^3} \right) \frac{1}{k^2 - (k')^2 \pm i\epsilon}, \end{aligned} \quad (2.1.11)$$

which we can integrate in spherical coordinates as

$$G_\pm(x, x') = - \int_0^\infty dk' (k')^2 \int_0^\theta d\theta \sin\theta \int_0^{2\pi} d\phi \frac{e^{i\vec{k}'\cdot(\vec{x}-\vec{x}')}}{(2\pi)^3} \frac{1}{k^2 - (k')^2 \pm i\epsilon} \quad (2.1.12)$$

Actually computing this integral involves noting that this integral is invariant under  $k' \rightarrow -k'$  so we can integrate by extending from  $-\infty \rightarrow \infty$  and dividing by 2. So we get that

$$G_\pm(x, x') = - \frac{1}{8\pi^2} \frac{1}{i|\vec{x}-\vec{x}'|} \int_{-\infty}^\infty dk' k' \frac{e^{ik'|\vec{x}-\vec{x}'|} - e^{-ik'|\vec{x}-\vec{x}'|}}{k'^2 - k^2 \pm i\epsilon} \quad (2.1.13)$$

We can perform this integral using residue theory. Note we have four poles and we can get the final solution by performing a contour integral. After this application, we get that

$$\boxed{G_\pm(x, x') = - \frac{1}{4\pi} \frac{e^{\pm ik|\vec{x}-\vec{x}'|}}{|\vec{x}-\vec{x}'|}} \quad (2.1.14)$$

which describes and outward and inward ( $\pm$ ) spherical wave. So now we can write the solutions to our differential equations

$$\boxed{\psi^\pm = \frac{1}{(2\pi)^3} e^{i\vec{k}\cdot\vec{x}} - \frac{2m}{\hbar^2} \int d^3x' \frac{e^{\pm ik|\vec{x}-\vec{x}'|}}{4\pi|\vec{x}-\vec{x}'|} V(x') \psi^\pm(x')} \quad (2.1.15)$$

We have obtained a complete iterative solution, however, it is useful to consider limiting behavior. If we make the local approximation that  $|\vec{x}| \gg |\vec{x}'|$ , then if we let  $|\vec{x}| = r$  and  $|\vec{x}'| = r'$  and  $\alpha$  is the angle between the two, then we can approximate

$$\begin{aligned} |\vec{x} - \vec{x}'| &= \sqrt{r^2 + r'^2 - 2rr' \cos \alpha} \\ &\approx r - r' \cos \alpha, \end{aligned} \quad (2.1.16)$$

where we have used the binomial approximation and  $r' \cos \alpha = \vec{x}' \cdot \hat{x}$ . So we can rewrite our solution as  $r \rightarrow \infty$  as

$$|\psi^+\rangle = \frac{e^{i\vec{k} \cdot \vec{x}}}{(2\pi)^{3/2}} - \frac{1}{4\pi} \frac{2m}{\hbar} \frac{e^{ikr}}{r} \int d^3x' e^{-i\vec{k}' \cdot \vec{x}'} V(x') \psi^+(x'), \quad (2.1.17)$$

which we can rewrite as

$$|\psi^+\rangle = \frac{1}{(2\pi)^{3/2}} \left[ e^{i\vec{k} \cdot \vec{x}} + \frac{e^{ikr}}{r} f(\vec{k}, \vec{k}') \right], \quad (2.1.18)$$

where  $f(\vec{k}, \vec{k}')$  is the scattering amplitude given as

$$\boxed{f(\vec{k}, \vec{k}') = -\frac{1}{4\pi} \frac{2m}{\hbar} (2\pi)^3 \langle \vec{k}' | V | \psi^+ \rangle}, \quad (2.1.19)$$

which is similar to a transition amplitude.

### 2.1.2 Overview of Formulation

IF we start with a beam along  $z$  axis of a single energy given as

$$E = \frac{\hbar^2 k^2}{2m}, \quad (2.1.20)$$

or  $E = h\nu$  for a photon, then we define  $j$  as the flux which is the number of particles covering unit area per unit time. What we often care about is the solid angle given as

$$d\Omega = \sin \theta d\theta d\phi, \quad (2.1.21)$$

or integrated over all solid angles. In general, we will scatter an incoming plane wave and scatter to a spherical wave. We are looking for solutions to a Schrodinger equation given as

$$(T + V)\psi = E\psi \quad (2.1.22)$$

where  $\psi$  are wavefunctions. We can have both elastic and inelastic scattering, however we will only deal with elastic scattering where a particle which goes into the scattering situation will come out with the same energy. The boundary conditions mean that

$$\psi|_{\text{long distance}} = e^{i\vec{k} \cdot \vec{x}} + \frac{e^{ikr}}{r} f(\theta, \phi), \quad (2.1.23)$$

which is the addition of a plane wave and a spherical wave. With this we can easily calculate the flux. It will turn out that the interference between the plane wave and the spherical wave is negligible, however, we need to prove this. We will find that

$$\boxed{\frac{d\sigma}{d\Omega} = |f(\theta, \phi)|^2}, \quad (2.1.24)$$

which implies that once we have a solution to the Schrodinger equation, it is easy to find cross section. We have obtained this in the previous section. This solution is often called  $\psi^+$ , called the Lippmann-Schwinger equation, and is given by

$$|\psi^+\rangle = |\vec{k}\rangle + \frac{1}{E - H_0 + i\epsilon} V |\psi^+\rangle, \quad (2.1.25)$$

where  $H_0 = T$ , the kinetic energy. Now if we define the  $T$ matrix as

$$T |\vec{k}\rangle = V |\psi_k^+\rangle \quad (2.1.26)$$

Now we can write the scattering amplitude as

$$f(\theta, \phi) = -\frac{1}{4\pi} \left( \frac{2m}{\hbar^2} \right) \langle \vec{k}' | T | \vec{k} \rangle, \quad (2.1.27)$$

which we can see by substitution of the Lippmann-Schwinger equation

$$\begin{aligned} T |\vec{k}\rangle &= V |\psi_k^+\rangle \\ &= V |\vec{k}\rangle + V \frac{1}{E - H_0 + i\epsilon} V |\psi_k^+\rangle \\ &= V |\vec{k}\rangle + V \frac{1}{E - H_0 + i\epsilon} T |\vec{k}\rangle, \end{aligned} \quad (2.1.28)$$

and so we can cancel  $|\vec{k}\rangle$ , we get the T-matrix equation

$$T = V + V \frac{1}{E - H_0 + i\epsilon} T. \quad (2.1.29)$$

When  $V$  is small, we can do perturbation theory with this. If we write

$$G_0^+ = \frac{1}{E - H_0 + i\epsilon}, \quad (2.1.30)$$

we can expand the  $T$ -matrix equation as

$$T = V + V G_0^+ V + V G_0^+ V G_0^+ V + \dots, \quad (2.1.31)$$

which has the physical meaning of interacting once, or interacting multiple times with Green's functions propagating in between the interaction.

## 2.2 Born Approximation

The Born approximation deals with the perturbation solution to the  $T$ -matrix equation and we approximate

$$T \approx V, \quad (2.2.1)$$

which is saying we approximate  $T$  by only the first term in its expansion. So we have that to first order Born approximation

$$f^{(1)}(\theta, \phi) = -\frac{1}{4\pi} \left( \frac{2m}{\hbar^2} \right) \langle \vec{k}' | V | \vec{k} \rangle, \quad (2.2.2)$$

which we can rewrite as

$$\begin{aligned}
f^{(1)}(\theta, \phi) &= -\frac{1}{4\pi} \left( \frac{2m}{\hbar^2} \right) \int e^{-i\vec{k}' \cdot \vec{r}} V(\vec{r}) e^{i\vec{k} \cdot \vec{r}} d^3\vec{r} \\
&= -\frac{1}{4\pi} \left( \frac{2m}{\hbar^2} \right) \int e^{-i(\vec{k}' - \vec{k}) \cdot \vec{r}} V(\vec{r}) d^3\vec{r} \\
&= -\frac{1}{4\pi} \left( \frac{2m}{\hbar^2} \right) \int e^{i\vec{q} \cdot \vec{r}} V(\vec{r}) d^3\vec{r},
\end{aligned} \tag{2.2.3}$$

where  $\vec{k}' - \vec{k} = \vec{q}$ , a momentum transfer. Noting the definition of a Fourier transform, we get that

$$\boxed{f^{(1)}(\theta, \phi) = \frac{1}{4\pi} \left( \frac{2m}{\hbar^2} \right) V(\vec{q})}. \tag{2.2.4}$$

So the scattering amplitude is related to the potential. So we can learn about the potential through the scattering.

### 2.2.1 Example: Yukawa Potential

Consider the potential

$$V(r) = \frac{V_0 e^{-\mu r}}{\mu r}, \tag{2.2.5}$$

which is a short interaction with interaction radius  $1/\mu$ . We can write

$$V(q) = \int \frac{V_0}{\mu} \frac{e^{-\mu r}}{r} d^3\vec{r} e^{i\vec{q} \cdot \vec{r}} \propto \frac{1}{q^2 + \mu^2}, \tag{2.2.6}$$

which we can use to write the cross section as

$$\boxed{\frac{d\Omega}{d\Omega} = \left( \frac{2mV_0}{\mu\hbar^2} \right)^2 \frac{1}{[2k^2(1 - \cos\theta) + \mu^2]^2}}. \tag{2.2.7}$$

As  $\mu \rightarrow 0$  with the appropriate limits, the Coulomb potential is recovered, and we can also recover the Rutherford cross section. We can also calculate this classically, so it is quite remarkable that the Born approximate recovers this by quantum mechanical means.

### 2.2.2 Validity of Born Approximation

It is useful to know when the Born approximation is valid. We know that we can write the full solution as

$$\psi^+ \approx e^{ikz} + \frac{e^{ikr}}{r} \left( -\frac{1}{4\pi} \frac{2m}{\hbar^2} \int e^{i\vec{q} \cdot \vec{r}} V(r) d^3\vec{r} \right) + \dots, \tag{2.2.8}$$

and in a general sense, the Born approximation is valid for a small potential. So we necessarily put  $q$  small, or else there is no scattering. The first term can be approximated as 1 and so we need to look at the second term for a scattering area of  $a$ . This is about

$$-\frac{1}{a} \left( \frac{1}{4\pi} \right) \frac{2m}{\hbar^2} V \cdot \left( \frac{4}{3} \pi a^3 \right) \ll 1, \tag{2.2.9}$$

which we will state as

$$\left(\frac{2m}{\hbar^2}a^2\right)V \ll 1, \quad (2.2.10)$$

and so we get that

$$\boxed{V \ll \frac{\hbar^2}{2m} \left(\frac{1}{a^2}\right)}. \quad (2.2.11)$$

We can contrast this to the condition for a bound state, which is

$$V_0 \frac{\hbar^2}{2m} \left(\frac{1}{a^2}\right), \quad (2.2.12)$$

and we see that the scattering potential has to be much smaller than the kinetic energy of a particle confined in a box of dimension  $a$ . When  $q$  is large, we will use the eikonal approximation. When  $k$  is large, the approximation gets better and the condition becomes

$$\frac{2m}{\hbar^2} \frac{|V_0|a}{k} \ln(ka) \ll 1. \quad (2.2.13)$$

If the Born approximation is not valid, we can always take the perturbation series to higher terms.

## 2.3 Partial Wave Expansion

### 2.3.1 Formalism

The partial wave expansion works for low-energy where the Born approximation may or may not be valid. Here we think of this plane wave as

$$e^{ikz} = \sum_{l=0}^{\infty} (2l+1) P_l(\cos \theta) i^l j_l(kr), \quad (2.3.1)$$

a sum of partial waves, where  $j_l$  is a spherical Bessel function.  $j_l$  can be shown to limit as

$$\lim_{r \rightarrow \infty} j_l(kr) = \frac{e^{i(kr - \pi l/2)} - e^{-i(kr - \pi l/2)}}{2ikr} \quad (2.3.2)$$

Now we notice that we can write the scattering amplitude as

$$f(\theta) \frac{e^{ikr}}{r} = \sum_{l=0}^{\infty} (2l+1) f_l P_l(\cos \theta) \frac{e^{ikr}}{r}, \quad (2.3.3)$$

and so we can write

$$\psi^+ = \sum_{l=0}^{\infty} (2l+1) P_l(\cos \theta) \left[ \frac{e^{-ikr}}{r} + (-1)^l (1 + 2ikf_l) \frac{e^{ikr}}{r} \right], \quad (2.3.4)$$

where the first term comes from the incoming wave and the second from the scattering. Since we know that particle number must be conserved, we can restrict  $1 + 2ikf_l$ , and in fact it must be  $e^{2i\delta_l}$ , so there is only a phase shift. So, we only need to find all the phase shifts and it is important to note that this is an *exact* answer. Luckily, for lower energies, there are only a few partial waves

that matter. This still works for high energy scattering, however, there are many partial waves and the calculation becomes not as useful.

Formally, we write

$$f_l = \frac{e^{2i\delta_l} - 1}{2ik}, \quad (2.3.5)$$

and so we can write

$$f(\theta, \phi) = \sum_l \frac{e^{2i\delta_l} - 1}{2ik} (2l+1) P_l(\cos \theta), \quad (2.3.6)$$

which we can use to find that

$$\sigma = 4\pi \sum_l \frac{(2l+1)}{k^2} \sin^2 \delta_l. \quad (2.3.7)$$

If we now go back to our initial Schrodinger equation

$$(T + V)\psi = E\psi, \quad (2.3.8)$$

then we can write

$$\psi^+ = \sum_{l=0}^{\infty} P_l(\cos \theta) R_l(kr) A_l, \quad (2.3.9)$$

and if we define  $u_l(kr) = r R_l(kr)$  as normal, we can get the normal radial equation. By matching the boundary conditions properly as  $r \rightarrow 0$  (finite) and  $r \rightarrow \infty$  ( $1/r \sin(kr - \pi l/2 + \delta_l)$ ), we can get our solution.

### 2.3.2 Infinitely Hard Sphere

Suppose we have a sphere with the potential

$$V = \begin{cases} \infty & r > R \\ 0 & r < R, \end{cases} \quad (2.3.10)$$

so the particle cannot get into the sphere, but there is no interaction outside the sphere. Classically, the cross section of the sphere is  $\pi R^2$ . Now we write  $\pi_l = 1/r u_l$  and then we can write

$$\frac{d^2 u_l}{dr^2} + \left( k^2 - \frac{2m}{\hbar^2} V - \frac{l(l+1)}{r^2} \right) u_l = 0, \quad (2.3.11)$$

as the Schrodinger equation for this system. We know that  $u_l(R) = 0$  is one boundary condition and for  $r > R$ , there is no potential, so we can rewrite our equation as

$$\frac{d^2 u_l}{dr^2} + \left( k^2 - \frac{l(l+1)}{r^2} \right) u_l = 0, \quad (2.3.12)$$

which is a free particle Schrodinger equation subject to the boundary conditions which can be solved by Bessel and Neumann functions  $j_l(kr)$  and  $n_l(kr)$ , and both are possible with our boundary conditions, since we don't have to consider the origin. So our solution is given as

$$\psi_l^{(+)} = a_l j_l(kr) + b_l n_l(kr). \quad (2.3.13)$$

We now must match our boundary conditions. We know that

$$\lim_{r \rightarrow \infty} r_l(kr) = \frac{1}{r} \sin \left( kr - \frac{\pi l}{2} \right) \quad (2.3.14)$$

$$\lim_{r \rightarrow \infty} n_l(kr) = \frac{-1}{r} \cos \left( kr - \frac{\pi l}{2} \right), \quad (2.3.15)$$

so we can compare this asymptotic solution

$$\frac{1}{r} \left[ a_l \sin \left( kr - \frac{\pi l}{2} \right) - b_l \cos \left( kr - \frac{\pi l}{2} \right) \right], \quad (2.3.16)$$

so we can see that comparing to the known dependence of  $\psi^+$ , then  $a_l \propto \cos \delta_l$  and  $b_l \propto \sin \delta_l$ , which gives us at the boundary  $r = R$

$$j_l(kR) \cos(\delta_l) - n_l(kR) \sin(\delta_l) = 0, \quad (2.3.17)$$

which implies that

$$\boxed{\tan \delta_l = \frac{j_l(kR)}{n_l(kR)}} \quad (2.3.18)$$

So if we look at the low energy scattering  $k \rightarrow 0$ , then we can see that

$$j_l(kr) \approx \frac{(kr)^l}{(2l+1)!!}, \quad (2.3.19)$$

and

$$n_l(kr) \approx -\frac{(2l-1)!!}{(kr)^{l+1}}, \quad (2.3.20)$$

which recovers the equation

$$\tan \delta_l \approx \frac{-(kR)^{2l+1}}{(2l+1)((2l-1)!!)^2}, \quad (2.3.21)$$

where we note that  $!!$  is a generalized factorial which is  $n(n-2)\cdots$  with different end conditions for even or odd. We see that in this limit, for  $l > 0$ ,  $\delta_l$  becomes vanishingly small. So we can see that  $\tan \theta_0 = -kR$  which for small  $k$  means that  $\delta_0 = -kR$ . So we can calculate the cross section as

$$\begin{aligned} \sigma &= \frac{4\pi}{\hbar^2} \sin^2 \delta_0 \\ &= \frac{4\pi}{\hbar^2} \sin^2 kR \\ &\boxed{\approx 4\pi R^2}, \end{aligned} \quad (2.3.22)$$

which different than the classical result, (its the whole surface area) since it sees the whole sphere and not the area of a slice. This is  $s$  wave scattering.

Conversely, if  $k \rightarrow \infty$ , we will need all  $l$  terms. Summing up many  $l$ , it turns out that  $\sigma = 2\pi R^2$ . This is not the classical result, and the difference has to do with the particle wave duality of quantum mechanics. Basically half of this is from classical scattering and half of this is from wave properties.



### 2.3.3 Square Well (Barrier)

Here we have a potential which is rectangular in the sense that

$$V = \begin{cases} V_0 & r < R \\ 0 & r > R, \end{cases} \quad (2.3.23)$$

where we allow  $V_0$  both positive and negative. This will change the sign of the phase shift. So we need to solve the Schrodinger equation for  $r < R$  and  $R > r$  in the low energy limit. In this case, we only need to consider the  $s$ -wave scattering.

We can write the Schrodinger equation for  $r < R$  as

$$\frac{d^2 u}{dr^2} + (E - V_0) \left( \frac{2m}{\hbar^2} \right) u = 0, \quad (2.3.24)$$

and if we assume that  $E > V_0$  (typical conditions), we can define

$$k'^2 = (E - V_0) \left( \frac{2m}{\hbar^2} \right), \quad (2.3.25)$$

then we have that

$$\frac{d^2 u}{dr^2} + k'^2 u = 0, \quad (2.3.26)$$

which we can solve as

$$u(r < R) = A \sin(k'r + c) = A \sin(k'r) \quad (2.3.27)$$

where we note that  $R(r) = u(r)/r$  so we must have  $u(r)$  vanish at zero, so  $c = 0$ .

For  $r > R$ , we just get a free Schrodinger equation, so

$$u(r > R) = B \sin(kr + \delta_0), \quad (2.3.28)$$

where  $k^2 = 2mE/\hbar^2$ .

Now we need to match these solutions by saying that the wavefunction and its derivative are continuous at  $r = R$ . So we say that  $u'/u$  is continuous (this gets rid of the constants). So we have that

$$k' \frac{\cos(k'R)}{\sin(k'R)} = k \frac{\cos(kR + \delta_0)}{\sin(kR + \delta_0)}, \quad (2.3.29)$$

which we can solve for  $\delta_0$  by writing this as

$$\tan(k'R) = \frac{k'}{k} \tan(kR + \delta_0), \quad (2.3.30)$$

which gives that

$$\boxed{\delta_0 = -kR + \tan^{-1} \left( \frac{k}{k'} \tan(k'R) \right)}. \quad (2.3.31)$$

In the limit that  $k \rightarrow 0$  if we note that  $\tan^{-1}(x) \approx x$  for small  $x$ , we get that

$$\delta_0 \approx -kR + \frac{k}{k'} \tan(k'R), \quad (2.3.32)$$

and now we can introduce the scattering length  $a$  as

$$a = \lim_{k \rightarrow 0} - \left( \frac{\delta_0}{k} \right), \quad (2.3.33)$$

and so we can write

$$\delta_0 = -ak, \quad (2.3.34)$$

in this limit. So we can write the cross section as

$$\boxed{\sigma = 4\pi a^2}. \quad (2.3.35)$$

Note that the scattering length can be both positive and negative if there is attraction or repulsion. We can also write

$$a = R - \frac{1}{k'} \tan(k'R), \quad (2.3.36)$$

and by looking at the definition of  $k'$  in the limit  $E \rightarrow 0$  ( $k \rightarrow 0$ ),

$$k' = \sqrt{\frac{-2mV_0}{\hbar^2}}, \quad (2.3.37)$$

and so if  $V_0 \rightarrow 0$ ,  $a \rightarrow 0$ , which we can see by Taylor expanding the tangent term. However, if we make  $V_0$  increasingly negative, the scattering length will also become negative and can even go to negative infinity when

$$k'R = \frac{\pi}{2}. \quad (2.3.38)$$

This condition corresponds to

$$V_0 = -\frac{\hbar^2 \pi^2}{8mR^2}, \quad (2.3.39)$$

which is precisely the highest energy where a bound state exists. The reason the scattering length is infinite is because incoming particles will be trapped into the bound state.

We will now let  $\alpha = k'$ . Note that this bound state can happen for

$$\alpha R = \frac{\pi}{2} + \pi n \quad (2.3.40)$$

Now we note that since the cross section for  $s$  wave scattering is given as

$$\frac{4\pi}{k^2} \sin^2 \delta_0, \quad (2.3.41)$$

then we have a maximum cross section at  $\pi/2$  and it diverges as  $k \rightarrow 0$ . Also note that at  $\delta_0 = \pi$ , the cross section goes to 0 and  $a = 0$ .

### 2.3.4 Low Energy Expansions

Now we want to look at

$$\begin{aligned} f_l &= \frac{e^{2i\delta_0} - 1}{2ki} \\ &= \frac{e^{i\delta_0}(e^{i\delta_0} - e^{-i\delta_0})}{2ki} \\ &= \frac{e^{i\delta_0} \sin(\delta_0)}{k} \\ &= \frac{1}{k \cot \delta_0 - ki}, \end{aligned} \quad (2.3.42)$$

which means that for low energy

$$k \cot \delta_0 = k \frac{\cos \delta_0}{\sin \delta_0} = \frac{k}{\sin \delta_0} = -\frac{1}{a}. \quad (2.3.43)$$

and it can be shown that  $k \cot \delta_0$  is an analytical function of  $E$ . This is very important since it can then be expanded as a Taylor series. So we can write

$$k \cot \delta_0 = -\frac{1}{a} + \frac{1}{2}r_0k^2 + \dots \quad (2.3.44)$$

where  $r_0$  is called the effective range. Now we note that

$$f_0 = \frac{1}{-1/a = ik}, \quad (2.3.45)$$

and so if we think of  $E$  (of which  $k$  is a function), as a complex function, then there is a pole at

$$-\frac{1}{a} = ik = i\sqrt{\frac{2mE}{\hbar^2}}, \quad (2.3.46)$$

and so if we square this we get that

$$-\left(\frac{1}{a}\right)^2 = \frac{2mE}{\hbar^2}, \quad (2.3.47)$$

and so there is a pole with negative energy. So as the scattering length goes to  $\infty$ , this pole goes to 0. So the bound state must go as  $\psi = e^{kr}/r$ . One can then argue the bound state wavefunction is not so different from the scattering solution since they are both approaching 0 from different axis in an imaginary plane. This says that small bound states have a huge effect on the scattering, but large bound states do not.

## 2.4 Resonance

Suppose that we have a potential well is deep, but not infinite on one side. Then we have no real bound states, but particles which have the same energy as a near bound state, then it will have a large cross section. So this is a resonance. The interaction time will also be very long (sort of like a metastable bound state).

For example, consider the hydrogen atom in the first excited state. Eventually this would decay (has finite lifetime). So we can think of this as a resonance between the ground state and a photon. Anything that is not stable is a resonance. Even a Neutron. From this point of view, only states with infinitely long lifetimes are bound states.

If we look at the effective potential for a central potential depending only on  $r$ , we have

$$V_{eff}(r) = V(r) + \frac{l(l+1)}{r^2}\hbar^2, \quad (2.4.1)$$

which can produce a resonance only if it is attractive. In addition, resonance can only occur at positive energy such that particle can eventually go to infinity. If we look at the partial wave scattering we get that

$$\sigma_l = \frac{4\pi}{k^2}(2l+1)\sin^2 \delta_l, \quad (2.4.2)$$

and since for a resonance, this becomes maximal, we know that the phase shift for a resonance, is at

$$\delta_l = \frac{\pi}{2}, \frac{3\pi}{2}, \dots, \quad (2.4.3)$$

and we can write

$$\sigma_l = \frac{4\pi}{k^2}(2l+1). \quad (2.4.4)$$

Spectroscopically the lifetime is short if resonance is broad if we are looking at  $\sigma_l$  vs  $E$  and lifetime is long if resonance is narrow. Both are difficult experimentally. So we want to find this lifetime.

### 2.4.1 Lifetime

We can generally fit the resonance to the Breit-Wigner form. We write

$$f = \frac{1}{k \cot \delta - ik}, \quad (2.4.5)$$

when there is a resonance,  $\delta \rightarrow \pi/2$  and so  $\cot \delta \rightarrow 0$ . Thus, we can expand  $\cot$  as

$$\cot \delta = (E - E_R)C + (E - E_R)^2\beta, \quad (2.4.6)$$

around the resonance energy  $E_R$ , which gives us

$$f = \left(\frac{1}{k}\right) \frac{1/c}{E - E_R - i/c}, \quad (2.4.7)$$

and if we define  $1/c = -\Gamma/2$ , then we have the scattering amplitude near the resonance as

$$f = \left(\frac{1}{k}\right) \frac{-\Gamma/2}{E - E_R + i\Gamma/2} \quad (2.4.8)$$

which gives us that

$$\sigma = \frac{4\pi}{k^2}(2l+1) \frac{(\Gamma/2)^2}{(E - E_R)^2 + (\Gamma/2)^2}, \quad (2.4.9)$$

which is a Lorentzian and called the Breit-Wigner form. So we can fit the function to data to extract relevant parameters. This only works for a specific  $l$ , so it gets complicated if there are many  $l$ .

## 2.5 High Energy Scattering

### 2.5.1 Eikonal Approximation

The situation is that we have a particle which travels with some impact parameter  $b$  with energy  $E \gg |V|$ , it has little deflection. So we consider scattering at small angle  $\theta$ . We define  $\vec{x}$  as the position after the scattering and  $z$  is the distance away from the center of the scattering (also  $x \cos \theta$ ).

We assume that  $V(\vec{x})$  varies very little over a distance of the order of the incoming wave. This is the semi-classical WKB approximation. On the other hand, because the particle almost travels in a straight line, this approximation is also called the straight line approximation.

Now we want to find a solution of the form

$$\psi^{(+)} = e^{iS(\vec{x})/\hbar}, \quad (2.5.1)$$

which we can plug into the time dependant Schrodinger equation

$$-\frac{\hbar^2}{2m}\nabla^2\psi^{(+)} + V\psi^{(+)} = E\psi^{(+)}, \quad (2.5.2)$$

where  $E = \hbar^2 k^2/2m$  which yields

$$\left(-\frac{i\hbar}{2m}\nabla^2 S(\vec{x}) + \frac{(\nabla S)^2}{2m} + V\right)\psi^{(+)} = E\psi^{(+)}, \quad (2.5.3)$$

we know that

$$\nabla^2 S(x)/2m \propto k'(z), \quad (2.5.4)$$

and

$$(\nabla S(x))^2/2m \propto |k(z)|^2. \quad (2.5.5)$$

So since  $|k'(z)| \ll |k(z)|^2$  in our approximation, we can ignore the first term. So we can write down our equation as

$$\frac{(\nabla S)^2}{2m} + V = E, \quad (2.5.6)$$

which is the Hamiltonian-Jacobi equation. We can reduce this to one variable since energy is high and there will be little  $x, y$  dependence. So we can write our equation as

$$\left(\frac{dS}{dz}\right)^2 = (E - V)2m, \quad (2.5.7)$$

which gives us the final form

$$\frac{dS}{dz} = \pm \left[ \hbar^2 \left( k^2 - \frac{2m}{\hbar^2} V \right) \right]^{1/2}, \quad (2.5.8)$$

and we can choose the root by looking at the boundary conditions. This will correspond to the positive root and so we have that

$$\frac{S(\vec{x})}{\hbar} = \int_{-\infty}^z dz' \sqrt{k^2 - \frac{2m}{\hbar^2} V} + C, \quad (2.5.9)$$

where  $C$  is some constant. We would like to set this constant to get the correct asymptotic behavior. We know that that  $\lim_{V \rightarrow 0} S/\hbar \rightarrow kz$ , which implies that

$$\int_{-\infty}^z dz' k + C = kz, \quad (2.5.10)$$

so we can solve for

$$C = kz - \int_{-\infty}^z dz' k, \quad (2.5.11)$$

where one must be careful about divergent infinities when solving for  $C$ , however, it will cancel when plugged back into the whole equation. So we have our full solution as

$$\frac{S}{\hbar} = \int_{-\infty}^z dz' \left[ \sqrt{k^2 - \frac{2mV}{\hbar^2}} - k \right] + kz \quad (2.5.12)$$

We now can make some approximation by noting that binomial expansion gives

$$\begin{aligned} \left(k^2 - \frac{2mV}{\hbar^2}\right)^{1/2} &= k \left(1 - \frac{2mV}{\hbar^2 k^2}\right)^{1/2} \\ &\approx k \left(1 - \frac{2mV}{2\hbar^2 k^2}\right) \\ &= k - \frac{mV}{\hbar^2 k^2}, \end{aligned} \quad (2.5.13)$$

and so we have that

$$\frac{S}{\hbar} = kz - \frac{m}{\hbar^2 k} \int_{-\infty}^z dz, V, \quad (2.5.14)$$

and our wavefunction is given as

$$\boxed{\psi^{(+)}(\vec{x}) = \psi^{(+)}(\vec{b} + z\hat{z}) = \frac{1}{(2z)^{3/2}} e^{ikz} \exp\left[-\frac{im}{\hbar^2 k} \int_{-\infty}^z dz' V(\sqrt{b^2 + z'^2})\right]} \quad (2.5.15)$$

Now we can find the scattering amplitude by using

$$f(\vec{k}, \vec{k}') = -\frac{1}{4\pi} \frac{2m}{\hbar^2} \int d^3x' e^{-i\vec{k}' \cdot \vec{x}'} V(\vec{x}') \psi^{(+)}(\vec{x}') \quad (2.5.16)$$

and so if we plug our solution in, we get the scattering amplitude as

$$f(\vec{k}, \vec{k}') = -\frac{1}{4\pi} \frac{2m}{\hbar^2} \int d^3x' e^{-i\vec{k}' \cdot \vec{x}'} V(\sqrt{b^2 + z'^2}) e^{i\vec{k} \cdot \vec{x}'} \exp\left[-\frac{im}{\hbar^2 k} \int_{-\infty}^{z'} dz'' V(\sqrt{b^2 + z''^2})\right] \quad (2.5.17)$$

We can evaluate this in cylindrical coordinates. We can make some approximations and write that

$$\begin{aligned} -\vec{k}' \cdot \vec{b} &= -(k \sin \theta \hat{x} + k \cos \theta \hat{z}) \cdot (b \cos \phi_b \hat{x} + b \sin \phi_b \hat{y}) \\ &= kb \sin \theta \cos \phi_b \\ &\approx kb \theta \cos \phi_b, \end{aligned} \quad (2.5.18)$$

and if we plug this into our equation for scattering amplitude,

$$f(\vec{k}', \vec{k}) = -\frac{1}{4\pi} \frac{2m}{\hbar^2} \int_0^\infty b db \int_0^{2\pi} d\phi_b e^{-ikb\theta \cos \phi_b} \int_{-\infty}^\infty dz' V(z') \exp\left[-\frac{im}{\hbar^2 k} \int_{-\infty}^{z'} dz'' V(z'')\right], \quad (2.5.19)$$

which we can evaluate. If we denote

$$\Delta(b) = -\frac{m}{2\hbar^2 k} \int_{-\infty}^\infty dz V(\sqrt{b^2 + z^2}), \quad (2.5.20)$$

the result can be simplified after the integration as

$$\boxed{f(\vec{k}', \vec{k}) = -ik \int_0^\infty db b j_0(kb\theta) (e^{2i\Delta(b)} - 1)}, \quad (2.5.21)$$

where  $j_0$  is the spherical Bessel function and in reality we change the outer limit to the limit of the scattering parameter.

This allows and easy proof of the optical theorem given as

$$\boxed{\int d\Omega |f|^2 = \frac{4\pi}{\hbar} \text{Im}[f(k, k)].} \quad (2.5.22)$$

### 2.5.2 High Energy Partial Waves

We know that

$$l = \frac{pb}{\hbar} = kb, \quad (2.5.23)$$

so we know that  $R \gg 1/k$  which implies that  $kR \gg 1$ . So it means that  $kb \gg 1$  and thus we need a large partial wave expansion. So we can approximate the sum of partial waves as an integral,

$$\sum_{l=0}^{kR} \rightarrow \int_0^{kR} d(kb), \quad (2.5.24)$$

and the Legendre polynomials will asymptote as

$$P_l(\cos \theta) \approx j_0(l\theta) = j_0(kb\theta), \quad (2.5.25)$$

do we write  $dl = \Delta(b)|_b = l/k$ . So now

$$\begin{aligned} f(k', k) &= \sum_{l=0}^{kR} (2l+1) \frac{e^{2idl} - 1}{2ik} P_l(\cos \theta) \\ &\approx \int_0^{kR} d(bk) \frac{2bk+1}{2ik} (e^{2i\Delta(b)} - 1) j_0(kb\theta) \\ &\approx -ik \int_0^\infty db b j_0(kb\theta) [e^{2i\Delta(b)} - 1], \end{aligned} \quad (2.5.26)$$

which is the same result we obtained for the Eikonal approximation, although formally, we need to solve for  $\Delta(b)$  to make sure it is the same as in the Eikonal approximation.

## 2.6 Inelastic Electron-Atom Scattering

Here we consider an electron scattering of an atom in its ground state. The product will be an electron and an atom in an excited state.

### 2.6.1 Formulation

We consider the initial state of the system  $|\vec{k}, 0\rangle$ , where  $\vec{k}$  is the momentum of the charged particle, and  $|0\rangle$  is the ground state of the atom. After scattering, the system exists in  $|\vec{k}', m\rangle$ , where  $|m\rangle$  is the excited state of the atom and

$$E_{k'} = \frac{\hbar^2 k'^2}{2m} < E_k = \frac{\hbar^2 k^2}{2m}. \quad (2.6.1)$$

So we write

$$\langle x_1, x_2, \dots, x_z | \vec{k}, 0 \rangle = e^{i\vec{k} \cdot \vec{x}} \psi_0(x_1, \dots, x_z), \quad (2.6.2)$$

for the initial state and for the final state

$$\langle x_1, x_2, \dots, x_z | \vec{k}, n \rangle = e^{i\vec{k}' \cdot \vec{x}} \psi_n(x_1, \dots, x_z) \quad (2.6.3)$$

Now we will use the Fermi Golden rule to calculate the transition rate which is given by the fermi golden rule

$$\frac{d^3 k'}{(2\pi)^3} \frac{2\pi}{\hbar} |\langle \vec{k}', n | V | \vec{k}, 0 \rangle|^2 \delta(E_k - E_{k'} - (E_n - E_0)) \quad (2.6.4)$$

With some algebra, we can write

$$k' = \sqrt{k^2 - \frac{2m}{\hbar^2}(E_n - E_0)}, \quad (2.6.5)$$

which allows us to rewrite the Fermi golden rule as

$$\frac{2\pi}{\hbar} |\langle \vec{k}', n | V | \vec{k}, 0 \rangle|^2 \frac{1}{(2\pi)^3} \frac{m_e k'}{\hbar^2} d\Omega, \quad (2.6.6)$$

where we have used the fact that

$$\delta(f(x)) = \delta(x) \frac{1}{|f'(x)|}. \quad (2.6.7)$$

Now we recall that the differential cross section is the transition rate per unit solid angle divided by the flux of the incoming charged particle. We can write the flux as

$$\vec{j} = \frac{\hbar \vec{k}}{m}, \quad (2.6.8)$$

a known result for a plane wave. So we can write

$$\frac{d\sigma}{d\Omega} = \frac{m}{\hbar k} \frac{2\pi}{\hbar} |\langle \vec{k}', n | V | \vec{k}, 0 \rangle|^2 \frac{1}{(2\pi)^3} \frac{m_e k'}{\hbar^2}, \quad (2.6.9)$$

which we can simplify as

$$\boxed{\frac{d\sigma}{d\Omega} = \frac{k'}{k} \left| \frac{m_e}{2\pi\hbar^2} \langle \vec{k}', n | V | \vec{k}, 0 \rangle \right|^2} \quad (2.6.10)$$

Note that this differs slightly from the book as we have used Dirac normalization instead of box normalization. So for the final result we need to calculate this matrix element.

## 2.6.2 Calculating Interaction Matrix Element

We can write the interaction as

$$V = -\frac{Ze^2}{\gamma} + \sum_i^Z \frac{e^2}{|\vec{x} - \vec{x}_i|}, \quad (2.6.11)$$

where  $\gamma = |\vec{x}|$ . Note that in general we would need to consider the electron scattering as indistinguishable particles and we would need to anti-symmetrize the wavefunction. However, in our case we can safely ignore this effect due to the plane wave nature of the incoming electron. Now we want to calculate

$$\begin{aligned} \langle \vec{k}', n | V | \vec{k}, 0 \rangle &= \int d^3x \prod_{i=1}^Z \int d^3x_i \langle \vec{k}', n | \vec{x}_1, \dots, \vec{x}_z \rangle \langle \vec{x}_1, \dots, \vec{x}_z | V | \vec{x}_1, \dots, \vec{x}_z \rangle \langle \vec{x}_1, \dots, \vec{x}_z | \vec{k}, 0 \rangle \\ &= \int d^3x e^{i\vec{k} \cdot \vec{x} - i\vec{k}' \cdot \vec{x}} \prod_{i=1}^Z \int d^3x_i \psi^*(\vec{x}_1, \dots, \vec{x}_z) \left( -\frac{e^2 Z}{\gamma} + \sum_{i=1}^Z \frac{e^2}{|\vec{x} - \vec{x}_i|} \right) \psi_0(\vec{x}_1, \dots, \vec{x}_z). \end{aligned} \quad (2.6.12)$$



So if denote  $\vec{q} = \vec{k} - \vec{k}'$ , we can simplify our equation as

$$\langle \vec{k}', n | V | \vec{k}, 0 \rangle = \int d^3x e^{i\vec{q}\cdot\vec{x}} \prod_{i=1}^z \int d^3x_i \psi^*(\vec{x}_1, \dots, \vec{x}_z) \left( -\frac{e^2 Z}{\gamma} + \sum_{i=1}^Z \frac{e^2}{|\vec{x} - \vec{x}_i|} \right) \psi_0(\vec{x}_1, \dots, \vec{x}_z). \quad (2.6.13)$$

Now we can calculate this integral term by term.

$$\left\langle \vec{k}', n \left| -\frac{Ze^2}{\gamma} \right| \vec{k}, 0 \right\rangle = \int d^3x e^{i\vec{q}\cdot\vec{x}} \left( -\frac{Ze^2}{|\vec{x}|} \right) \langle n | 0 \rangle = -Ze^2 \frac{4\pi}{q^2} \delta_{n0}, \quad (2.6.14)$$

which means we only get scattering from the save state for this term. For the next term, we have

$$\begin{aligned} \int d^3x e^{i\vec{q}\cdot\vec{x}} \left\langle n \left| \sum_{i=1}^Z \frac{e^2}{|\vec{x} - \vec{x}_i|} \right| 0 \right\rangle &= \int d^3x \left\langle n \left| \sum_{i=1}^Z \frac{e^2 e^{i\vec{q}\cdot\vec{x}}}{|\vec{x} - \vec{x}_i|} \right| 0 \right\rangle \\ &= \left\langle n \left| e^2 \sum_{i=1}^Z \int d^3x \frac{e^{i\vec{q}\cdot\vec{x}}}{|\vec{x} - \vec{x}_i|} \right| 0 \right\rangle. \end{aligned} \quad (2.6.15)$$

If we change variables, we cna write this as

$$\frac{4\pi e^2}{q^2} \left\langle n \left| \sum_{i=1}^Z e^{i\vec{q}\cdot\vec{x}_i} \right| 0 \right\rangle, \quad (2.6.16)$$

and we can define

$$\rho_{atom}(\vec{x}) = \sum_i^Z \delta^{(z)}(\vec{x} - \vec{x}_i), \quad (2.6.17)$$

and note that

$$\int d^3x e^{i\vec{q}\cdot\vec{x}} \rho_{atom} = \sum_{i=1}^Z e^{i\vec{q}\cdot\vec{x}_i}, \quad (2.6.18)$$

and so by defining the form factor

$$ZF_N(\vec{q}) \left\langle n \left| \sum_{i=1}^Z e^{i\vec{q}\cdot\vec{x}_i} \right| 0 \right\rangle, \quad (2.6.19)$$

we can study this in limit  $\vec{q} \rightarrow 0$ , which gives elastic scattering.

So for  $\vec{q} \neq 0$ , we have that

$$\int d^3x e^{i\vec{q}\cdot\vec{x}} \left\langle n \left| -\frac{Ze^2}{\gamma} + \sum_{i=1}^Z \frac{e^2}{|\vec{x} - \vec{x}_i|} \right| 0 \right\rangle = \frac{4\pi Ze^2}{q^2} (-\delta_{n0} + F_n(\vec{q})), \quad (2.6.20)$$

which allows us to write

$$\boxed{\frac{d\sigma}{d\Omega} = \frac{4m_e}{\hbar^4} \frac{(Ze^2)^2}{q^4} \frac{k'}{k} |-\delta_{n0} + F_n(\vec{q})|^2} \quad (2.6.21)$$

We can simplify this by introducing the Bohr radius and if we also assume  $n \neq 0$ , we get

$$\frac{d\sigma}{d\Omega} = 4Z^2 \frac{k'}{k} \frac{1}{q^4 a_0^2} |F_n(\vec{q})|^2. \quad (2.6.22)$$

Often experimentalists are interested in  $d\sigma/dq$ , which after some simplification, we can write

$$\boxed{\frac{d\sigma}{dq} = \frac{2\pi q}{kk'} \frac{d\sigma}{d\Omega}} \quad (2.6.23)$$

## 3 Identical Particles

Often we have systems with identical particles, such as two electrons, multiple atoms, etc. We need to learn to deal with them quantum mechanically.

### 3.1 Formulation

To simplify the problem, we are going to consider  $N$  particles which are all the same. We have some Hamiltonian which is a function of the particles, however, it must be independent of the labels. This permutation symmetry gives rise to permutation symmetry group  $S_n$ . We will denote the permutation of 1, 2 as  $P_{1,2}$ . We can write this as the matrix

$$P_{1,2} = \begin{pmatrix} 1 & 2 & 3 & \dots & n \\ 2 & 1 & 3 & \dots & n \end{pmatrix} \quad (3.1.1)$$

These permutations form a group. Can prove closure, etc.

So if we have the Schrodinger equation

$$H\psi(\vec{r}_1, \dots, \vec{r}_n) = E\psi(\vec{r}_1, \dots, \vec{r}_n), \quad (3.1.2)$$

then there are  $n!$  wavefunctions which are permutations of the coordinates and all are degenerate. However, not all of these states are necessarily physical. This is because if we examine the wavefunction  $\psi(\vec{r}_1, \dots, \vec{r}_n)$ , and we calculate probability density

$$|\psi(\vec{r}_1, \dots, \vec{r}_n)|^2 = P(\vec{r}_1, \dots, \vec{r}_n), \quad (3.1.3)$$

which is a physical observable and must be independent of what permutation we choose for the particle. This is known as indistinguishability. So this means that

$$\psi(1, \dots, n) = e^{i\alpha} P\psi(1, \dots, n), \quad (3.1.4)$$

where  $P$  is a permutation operator and therefore,  $e^{i\alpha} = \pm 1$  in order to satisfy the indistinguishability. So for any ideal particle system, it will either be totally symmetric, or totally anti-symmetric. This defines Bose and Fermi systems respectively.

It can be shown from Quantum field theory that spin half integer must be Fermi system, whereas spin integer system must be Bose system.

### 3.2 Symmetrizing and Anti-symmetrizing

#### 3.2.1 Two Particles

Suppose there are two particles which are in  $j_1$  and the other are in  $j_2$ . So we can write these as  $|j_1, m_1\rangle$  and  $|j_2, m_2\rangle$ . If we start with two of the same states, we can have

$$|j, j\rangle \otimes |j, j\rangle \implies J = j_2; m = 2j, \quad (3.2.1)$$

and so this state is symmetric since we can switch particle labels. We can generate the other  $m$  states by applying the lowering operator. We note that this is symmetric and therefore maintains the symmetry of the problem. We can also conclude the maximum angular momentum must be positive. Now if we lower the  $J$ , we get a antisymmetric state, then a symmetric state, etc.

### 3.2.2 Three Particles

If we have three particles, we can consider the maximal state  $|jjj\rangle$ . This state will have total angular momentum  $J = 3j$  and  $m = 3j$ .

## 3.3 Fermi Fluid

We consider a system of Fermi atoms where we can separate the inner and outer electrons and each atom contributes a valence electron to the fluid. These electrons move around like a gas inside the positive charge background of the nuclei. So we have a potential

$$V(x, y, z) = \begin{cases} -V_0 & 0 < X, Y, Z < L \\ 0 & \text{else} \end{cases} \quad (3.3.1)$$

where  $L$  is the dimension of the system assuming it is a box. We can solve for the energy levels in the well as

$$\frac{\hbar^2}{2m}(k_x^2 + k_y^2 + k_z^2), \quad (3.3.2)$$

and  $k = 2\pi n/L$ . So in the ground state, the electrons will try to fill these states and there will be two in each level to a particular energy. The highest energy minus the lowest energy is the Fermi Energy  $E_F$ . We want to know what the Fermi energy is in a particular metal. To count the number of states, we can write

$$N = \int \frac{d^3\vec{r}d^3\vec{p}}{h^3}, \quad (3.3.3)$$

and if we transform  $\vec{p} = \hbar\vec{k}$ , then we have that

$$N = \frac{2V}{(2\pi)^3} \int d^3\vec{k} = 2 \frac{V}{(2\pi)^3} \left( \frac{4}{3}\pi k_F^3 \right), \quad (3.3.4)$$

which is the volume of a sphere in wavevector (momentum) space. This is often called a Fermi sphere. The factor of two comes from the spin being allowed to be up or down. To calculate total energy, we can sum over the momentum inside the Fermi sphere

$$\begin{aligned} E &= \sum_{\vec{k}} \frac{\hbar^2 k^2}{2m} \\ &= \frac{2V}{(2\pi)^3} \int \left( \frac{\hbar^2 k^2}{2m} \right) d^3\vec{k} \\ &= \frac{2V}{(2\pi)^3} \left( \frac{\hbar^2}{2m} \right) 4\pi \int_0^{k_F} k^2(k^2 dx) \\ &= \frac{2V}{(2\pi)^3} \left( \frac{\hbar^2}{2m} \right) \frac{4\pi}{5} k_F^5 \\ &= N \left( \frac{\hbar^2}{2m} \right) \frac{3}{5} k_F^2 \\ &= \frac{3}{5} N E_F \end{aligned} \quad (3.3.5)$$

This implies that  $E/N = 3/5 E_F$ .

We now define the Fermi temperature, which is the temperature for which  $k_B T_F = E_F$ . We can extract this by looking at

$$N = \frac{V}{3\pi^2} k_F^3 \implies k_F = (3\pi^2 \rho)^{1/3}, \quad (3.3.6)$$

where  $\rho$  is the number density  $N/V$ . So then we know that

$$E_F = \frac{\hbar^2}{2m} \left( 3\pi^2 \frac{N}{V} \right)^{2/3} \quad (3.3.7)$$

So for many gases, we get a Fermi temperature of something like  $10^4$  Kelvin.

### 3.4 Z Electron Atoms

We consider an atom with  $Z$  electrons with a Hamiltonian given as

$$H = \sum_{i=1}^Z \frac{p_i^2}{2m} - \sum_{i=1}^Z \frac{Ze^2}{r_i} + \sum_{i < j=1}^Z \frac{e^2}{r_{ij}} \quad (3.4.1)$$

In general we cannot solve this problem, and so we will resort to a mean field theory. So we consider one electron with a Schrodinger equation given as

$$\left( \frac{p^2}{2m} + V(r) \right) \psi = E\psi, \quad (3.4.2)$$

where the potential  $V(r)$  is a mean field which is given by the other electrons. We then place the other electrons in this potential, recalculate  $V(r)$ , then iterate. This is called the Hartree-Fock equation. This picture means that the complicated atom still has a shell structure.

#### 3.4.1 Ground States of Atoms

We can write the atoms in their ground states as fairly easily, For the case where the  $P$  shell is partially filled, we can use Hund's rule which says that if the shell is less than half filled, one should take the lowest angular momentum value of the ground state.

For the Carbon atom, we have two electrons in the  $P$  state, so we have four angular momentum (two spin, two orbital). We can get the ground state by considering that if we symmetrize the spatial electron wavefunction, they will want to be close to each other, however, if we anti-symmetrize each other, they won't want to be as close. So in this case there will less Coulomb energy. In this case, the only antisymmetric state is where  $L = 1$ . So we need the electronic wavefunction to be symmetric, which means  $S = 1$ . Now we need to take  $J = 0$ , since the shell is half filled, so we should take the lowest total angular momentum. So the ground state of carbon is  $^3P_0$ .

The next element is Nitrogen. We have three electrons in the  $P$  shell, and so we have six angular momentum to couple. Again, we want the electrons to all be different states, so we have total anti-symmetry, where the electrons are all in different  $m$  sublevels. So  $L = 0$ . Now we need the spin part to be totally symmetric. So we need all the spins to be aligned and so  $S = 3/2$  and thus  $J = 3/2$ . So the ground state of Nitrogen is  $^4S_{3/2}$ .

Oxygen, is very similar to Carbon, since there is symmetry between holes and filled. The only difference is the Hund's rule. So the ground state is  $^3P_2$ .

### 3.4.2 He Nucleus

Here we have two protons and a Neutron. The orbital part is simple, we can write it as something like

$$e^{-(r_1^2+r_2^2+r_3^2)/b}, \quad (3.4.3)$$

However, the spin part is difficult because of the Heisenberg isospin symmetry spin the protons and neutrons have almost the same mass. The isospin is an abstract 2d space, where we consider protons spin up and neutrons spin down. So we can write

$$|p\rangle \sim \begin{pmatrix} 1 \\ 0 \end{pmatrix}; |n\rangle \sim \begin{pmatrix} 0 \\ 1 \end{pmatrix}, \quad (3.4.4)$$

and so this is the idea that the proton and neutron are essentially the same up to isospin. This is the first example of internal symmetries including things like color or flavor.

We know in the He nucleus we have two protons and we need an antisymmetric wavefunction. So we need the spin part the singlet function

$$(|p \uparrow p \downarrow\rangle - |p \downarrow p \uparrow\rangle) |n \uparrow\rangle + \text{anti-symmetrization} \quad (3.4.5)$$

which gives total angular momentum 0 and so if we couple in a neutron either up or down, we get  $J = 1/2$ . We need to anti-symmetrize with the neutron due to the isospin symmetry. So they are sort of quasi-identical particle.

### 3.4.3 Local Denisty Approximation (Thomas-Fermi)

When  $Z$  gets large, the nuclei get close together and  $k_F$  gets large. So the semi-classical approximation becomes quite good since the wavefunction has a very large frequency in position space. So this is also called a semi-classical approximation. It is not completely classical because we still have Fermi-Dirac statistics, however, near the Fermi surface, we can treat the particles as classical.

Mor formally, we treat the atom as spherically symmetric, with some density function  $\rho(r)$ . So we write the Fermi momentum as

$$k_F = (3\pi^2\rho)^{1/3}, \quad (3.4.6)$$

and we can write the energy as

$$E_0(r) = \frac{\hbar^2}{2\mu} k_F^2 + V(r), \quad (3.4.7)$$

where  $V(r)$  comes from the electrostatic interactions between the particles. Now since we are treating the whole atom as a classical charge distribution, we can use Poisson's equation which says that

$$\nabla^2 V = -4\pi e^2 \rho(r). \quad (3.4.8)$$

So if we use the fact that  $V = E_0 - \hbar^2 k_F^2 / 2\mu$ , we have

$$-\nabla^2 \left( \frac{\hbar^2}{2m} k_F^2(r) \right) = 4\pi e^2 \frac{1}{3\pi^2} k_F^3. \quad (3.4.9)$$

So if we now introduce kinetic energy as  $T = \frac{\hbar^2 k_F^2}{2\mu}$ , then we have

$$\left( \frac{d}{dr^2} + \frac{2}{r} \frac{d}{dr} \right) T = \frac{4e^2}{3\pi} \left( \frac{2\mu}{\hbar^2} T \right)^{3/2} \quad (3.4.10)$$

So if we introduce new variables  $\chi = rT/Ze^2$ ,  $x = r/b$  and

$$b = a_0 Z^{-1/3} \left( \frac{a_0 \pi^2}{128} \right)^{1/3}, \quad (3.4.11)$$

then we arrive at

$$\boxed{\frac{d^2 \chi}{dx^2} = \frac{\chi^{3/2}}{\sqrt{x}}} \quad (3.4.12)$$

and so the boundary conditions are that at  $x = 0$ ,  $\chi = 1$  and for small  $x$ , we can expand in a power series as

$$\chi(x) = 1 + Bx + \frac{4}{3}x^{3/2} + \dots, \quad (3.4.13)$$

and we also need to normalize such that

$$Z = 4\pi \int_0^\infty \rho(r) r^2 dr = Z. \quad (3.4.14)$$

This says that every atom looks the same at large  $Z$  and we can get the profile by numerical solutions to this equation.