

Phys 3820 (Quantum Mechanics) Notes

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Chapter 1

Time-Independent Perturbation Theory

1.1 Generalities

1.2 Non-Degenerate Perturbation Theory

For a problem where the unperturbed state (say, the n^{th} state) is *non-degenerate*, we can show:

The first-order correction to the energy is

$$E_n^1 = \langle \psi_n^0 | H' | \psi_n^0 \rangle \quad (1.1)$$

The first-order correction to the wave function is given by the (infinite) linear combination of the unperturbed wave functions:

$$\psi_n^1 = \sum_{m \neq n} \frac{\langle \psi_m^0 | H' | \psi_n^0 \rangle}{(E_n^0 - E_m^0)} \psi_m^0 \quad (1.2)$$

The second-order correction to the energy eigenvalue is given by:

$$E_n^2 = \sum_{m \neq n} \frac{|\langle \psi_m^0 | H' | \psi_n^0 \rangle|^2}{E_n^0 - E_m^0} \quad (1.3)$$

Note that for in the sums in 1.2 and 1.3 the denominators cannot be zero because by assumption, for the state ψ_n^0 there are no other states ψ_m^0 with the same energy.

1.3 Perturbation Theory for Degenerate States

For a state ψ_n^0 of the original system that is a member of a set of degenerate states, the procedures used to get 1.1, 1.2, and 1.3 are flawed. The problem arises from the fact that for a *pre-chosen* set of degenerate states, any linear combination is also an eigenfunction of the Hamiltonian H^0 and our original set of states may not be the “right” one as far as the perturbation is concerned.

What does *that* mean? It means that if our original unperturbed degenerate states were ψ_a^0 and ψ_b^0 , then applying the perturbation will give some other eigenstates but these new ones may *not* be just a wee bit different from ψ_a^0 and ψ_b^0 individually, rather they will be just a wee bit different from

Bohr energies	Coulomb potential of proton	$\alpha^2 mc^2$
Fine structure	Relativity and Spin–Orbit	$\alpha^4 mc^2$
Lamb Shift	QED	$\alpha^5 mc^2$
Hyperfine splitting	Interaction of proton and electron spins	$(m/m_p)\alpha^4 mc^2$

Table 1.1: Corrections to the energies of the H atom states.

some *linear combination* of the two. We mean that the correct starting point for the discussion of perturbations is a particular linear combination of the form

$$\psi_0 = \alpha\psi_a^0 + \beta\psi_b^0$$

$$W_{ij} \equiv \langle i|H'|j\rangle \quad (1.4)$$

1.4 Application to the H Atom

The basic treatment of the H atom given in Chapter 4 is good only as a first pass; the energies of the states must be corrected for effects arising from the spins of the electron and proton, the need for a relativistic theory and from consequences of the full theory of photons and electrons, “QED”. There is a hierarchy of

1.4.1 Fine Structure of H Atom

There are two corrections to H which give changes to E of the same order and are grouped together (here) as “fine structure”. One correction is the need to use relativistic dynamics and the other is a new effect called the **spin–orbit interaction**. Both physical corrections are built into the Dirac equation for the electron, but with our treatment we must put them in “by hand”.

The first correction is for the fact that the kinetic operator in the Schrödinger equation is based on the nonrelativistic formula $T = \frac{1}{2}mv^2 = \frac{p^2}{2m}$, which is not true in relativistic dynamics—it needs a correction which admittedly is small for the kinetic energy of a H atom electron. From a basic *algebraic* Taylor expansion of the expression for the relativistic kinetic energy, we find that the Hamiltonian needs a correction term

$$H'_r = -\frac{p^4}{8m^3c^2}$$

We associate the usual operator $\frac{\hbar}{i}\nabla$ with the \mathbf{p} of this expression to get a lowest–order correction for relativistic kinematics. It turns out that this correction *by itself* gives an energy correction of

$$E_r^1 = -\frac{(E_n)^2}{2mc^2} \left[\frac{4n}{l+1/2} - 3 \right]$$

but since it is of the same order as the upcoming “spin–orbit” correction, we don’t examine it yet...

A less obvious correction to the Hamiltonian comes from the interaction with the intrinsic magnetic moment of the electron with the electromagnetic field from the proton which it “sees”. If we make the treacherous of going the rest frame of the electron we have a proton orbiting the electron and as such it clearly generates a magnetic field at the location of the electron and the magnetic moment has an interaction with this field according to our usual relation $H = -\boldsymbol{\mu} \cdot \mathbf{B}$.

The B field from the proton is proportional to that angular momentum of the motion, \mathbf{L} and the magnetic moment is proportional to the spin angular momentum \mathbf{S} , so that the Hamiltonian correction should be proportional to $\mathbf{L} \cdot \mathbf{S}$ and one can eventually show (though it is far from clear at the level of the text) the correction to the Hamiltonian is

$$H'_{\text{so}} = \left(\frac{e^2}{8\pi\epsilon_0} \right) \frac{1}{m^2 c^2 r^3} \mathbf{S} \cdot \mathbf{L}$$

The H atom states of course have lots of degeneracy, but we can treat this perturbation in a simple way (with $E^1 = \langle \psi | H' | \psi \rangle$) if we choose states which are “good” for the operator $\mathbf{L} \cdot \mathbf{S}$. From the fact that

$$\mathbf{L} \cdot \mathbf{S} = \frac{1}{2}(J^2 - L^2 - S^2)$$

it follows that such states are also eigenstates of J^2 and J_z , and can be constructed with the Clebsch–Gordan coefficients of Chapter 4, though there will be no need for that here. We just *find* the energy correction to the state with quantum numbers n l and j . The result for the the energy correction due tho the spin–orbit effect is

$$E_{\text{so}}^1 = \frac{(E_n)^2}{mc^2} \left\{ \frac{n[j(j+1) - l(l+0) - 3/4]}{l(l+1/2)(l+1)} \right\} \quad (1.5)$$

This relativistic and spin–orbit corrections are of the same order, collectively known as **fine structure**. Combining the two corrections gives

$$E_{\text{so}}^1 = \frac{(E_n)^2}{2mc^2} \left(3 - \frac{4n}{j+1/2} \right) \quad (1.6)$$

so the the corrected energy levels of the H atom (now dependent on n and j) are

$$E_{nj} = -\frac{13.6 \text{ eV}}{n^2} \left[1 + \frac{\alpha^2}{n^2} \left(\frac{n}{j+1/2} - \frac{3}{4} \right) \right] \quad (1.7)$$

Thus the fine structure effects break the degeneracy in l but not the degeneracy in j within each of the sets of states indexed by n . At this level, the stationary states are those with “good” quantum numbers

$$n, l, s, j, \text{ and } m_j$$

When we use a fully relativistic wave equation (the Dirac equation) for the electron moving in the Coulomb field of a point charge, we get a result which incorporates relativity and the spin-orbit interaction in an *exact* sense. The result is:

$$E_{nj} = mc^2 \left\{ \left[1 + \left(\frac{\alpha}{n - (j+1/2) + \sqrt{(j+1/2)^2 - \alpha^2}} \right)^2 \right]^{-1/2} - 1 \right\} \quad (1.8)$$

which we note also depends on the quantum numbers n and j . As one can show in Problem 6.19, to lowest order in α^2 we recover Eq. 1.7.

Recall that even with the exact solution to the Dirac equation, we don’t include the correction of QED (“Lamb shift”) and the hyperfine splitting.

1.5 The Zeeman Effect

When an atom is placed in an external magnetic field \mathbf{B}_{ext} there are shifts in the energy levels; the shifts are known as the **Zeeman effect**. The perturbation in the electron's Hamiltonian is

$$H'_Z = -(\boldsymbol{\mu}_l + \boldsymbol{\mu}_s) \cdot \mathbf{B}_{\text{ext}}$$

where

$$\boldsymbol{\mu}_s = -\frac{e}{m}\mathbf{S} \quad \text{and} \quad \boldsymbol{\mu}_l = -\frac{e}{2m}\mathbf{L}$$

which gives

$$H'_Z = \frac{e}{2m}(\mathbf{L} + 2\mathbf{S}) \cdot \mathbf{B}_{\text{ext}}$$

There are two cases to distinguish; since there is already an internal magnetic field “felt” by the orbiting electron (which gave the fine structure) the external could be smaller or larger than what's already there! If these fields of comparable strength then things get messy; it's cleaner to consider the cases where the external field is much smaller than the internal one and then where it is much larger. These are the “weak” and “strong” Zeeman effects.

1.5.1 Weak-Field Zeeman Effect

Here, since the internal field is stronger the “good” quantum states are those of definite j and m_j . One can show that for an H atom state of total angular momentum j we have

$$\langle \mathbf{L} + 2\mathbf{S} \rangle = \left[1 + \frac{j(j+1) - l(l+1) + 3/4}{2j(j+1)} \right] \langle \mathbf{J} \rangle \equiv g_J \langle \mathbf{J} \rangle \quad (1.9)$$

which gives a correction to the energy levels of

$$E_Z^1 = \mu_B g_J B_{\text{ext}} m_j \quad \text{where} \quad \mu_B \equiv \frac{e\hbar}{2m} = 5.788 \times 10^{-5} \text{ eV/T} \quad (1.10)$$

This effect will split the ground state into two levels with energies given by

$$-13.6 \text{ eV}(1 + \alpha^2) \pm \mu_B B_{\text{ext}}$$

1.5.2 Strong-Field Zeeman Effect

Here the spin-orbit interaction is the smaller effect so that the states we consider have definite L_z and S_z . Now the Zeeman Hamiltonian is

$$H'_Z = \frac{e}{2m} B_{\text{ext}} (L_z + S_z)$$

which is a simple operator, and so the energy levels *without* the fine structure are

$$E_{nm_l m_s} = -\frac{13.5 \text{ eV}}{n^2} + \mu_B B_{\text{ext}} (m_l + 2m_s)$$

but if we now want to put in the fine structure contribution we have to put it in terms of m_l and m_s . One can show that its contribution can be expressed as

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

1.6 Hyperfine Splitting

We return to the H atom for a correction to the Hamiltonian which involves the spin of the proton. We recall that in between this correction and our previous work on the “fine structure” correction there was a correction due to the quantization of the EM field. But there is no way to treat this correction within the scope of the book so we omit it and go on to study the smaller correction of the **hyperfine splitting** effect.

This correction deals with the interaction of the magnetic moments of the proton and electron. One might think that this is a sizeable effect, but it is small because the magnetic moment of the proton is much smaller than that of the electron. Essentially this is due to the much larger mass of the proton.

The magnetic moments of the electron and proton are related to their spins by:

$$\boldsymbol{\mu}_p = \frac{g_p e}{2m_p} \mathbf{S}_p \quad \boldsymbol{\mu}_e = \frac{e}{m_e} \mathbf{S}_e \quad (1.11)$$

$$E_{\text{hf}}^1 = \frac{\mu_0 g_p e^2}{3\pi m_p m_e a^3} \langle \mathbf{S}_p \cdot \mathbf{S}_e \rangle \quad (1.12)$$

$$E_{\text{hf}}^1 = \frac{4g_p \hbar^4}{3m_p m_e^2 c^2 a^4} \begin{cases} +1/4 & (\text{triplet}) \\ -3/4 & (\text{singlet}) \end{cases} \quad (1.13)$$

At last we have an effect which splits the ground state in hydrogen, giving an energy gap between the (1s) singlet and triplet spin states of

$$\Delta E = \frac{4g_p \hbar^4}{3m_p m_e^2 c^2 a^4} = 5.88 \times 10^{-6} \text{ eV} \quad (1.14)$$

and a photon emitted for a transition between the two states has frequency

$$\nu = \frac{\Delta E}{h} = 1420 \text{ MHz}$$

or a wavelength of 21 cm, which falls in the microwave region of the EM spectrum. This particular “line” is thus a very prominent form of radiation in the universe.

Chapter 2

The Variational Method

2.1 Generalities

The primary theorem of this chapter is: For any quantum system (with Hamiltonian H , choose a wave function ψ which is normalized and satisfies all the proper boundary conditions. Then if E_{gs} is the ground state energy, then

$$E_{\text{gs}} \leq \langle \psi | H | \psi \rangle \equiv \langle H \rangle$$

This rule is used to get a *guaranteed upper bound* on the ground states energy of a system. It is called the **variational principle**. To make use of it, we choose a **trial function** ψ which we have reason to suppose is a reasonable approximation to the ground state wave function, and then evaluate $\langle H \rangle$ with this wave function. As our choices for ψ improve, the value of $\langle H \rangle$ gets closer to the true value of E_{gs} .

2.2 Application: Ground State of Helium

One of main applications of the variational principle in this chapter is the ground state of the helium atom. For this two-electron system (assume the nucleus to be at rest) the electron–electron repulsion in the Hamiltonian

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

prohibits a simple analytic solution. If we didn't have the e-e repulsion term, the ground state would be a simple product of hydrogenic wave functions for a central charge of $+2e$,

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

which would give (again without e-e repulsion) an energy of

$$E = 8E_1 = -109 \text{ eV}$$

as compared with the experimental energy of -78.795 eV .

What we can do is to take the above wave function $\psi_0(\mathbf{r}_1, \mathbf{r}_2)$ and treat it as a *trial* wave function for use with the variational principle. That will give us an upper bound for the true ground state energy. We find

$$H\psi_0 = (8E_1 + V_{ee})\psi_0 \quad \text{so then} \quad \langle H \rangle = 8E_1 + \langle V_{ee} \rangle$$

where

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

This integral can in fact be done exactly and one finds

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

giving a ground state upper bound of

$$\langle H \rangle = -109 \text{ eV} + 34 \text{ eV} = -75 \text{ eV}$$

We can get a better (i.e. lower) upper bound if we give the trial wave function a parameter that we can vary. In the above case we can consider a product of hydrogenic wave functions that would go with a central charge of $+Ze$. (We are free to do this though it does not change the fact that in the Hamiltonian H the terms go with a central charge of $+2e$.) Thus we use a trial wave function

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

one can show that for this trial function we get

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

where one gets

$$\left\langle \frac{1}{r} \right\rangle = \frac{Z}{a} \quad \text{and} \quad \langle V_{ee} \rangle = -\frac{5Z}{4} E_1$$

and with this, one can show

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

which has a minimum value for $Z = 1.69$, for which we get $\langle H \rangle = -77.5$, which gets us significantly closer to the experimental value.

This result has a nice interpretation: The electrons in helium in some ways behave as they do in the H atom but with a smaller *effective* nuclear charge. The reduced value is due to the fact that the second electron will partially “screen” the nuclear charge from the first electron.

2.3 Application: H_2^+ Molecule Ion

Another simple (and realistic) quantum system is that of the bound system of two protons and one electron, which form the H_2^+ molecular ion.

To make any progress we make the assumption that the protons remain at a fixed distance from one another and then work in a frame where the protons are at rest. The assumption that the electron motion in a molecule is “fast” compared to that of the nuclei is reasonable and goes by

the name of the **Born–Oppenheimer approximation** but like anything else, it should be kept in mind and questioned... later.

Here the complication in finding solution is that the one electron is attracted to *two* centers of force:

$$H = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0}\left(\frac{1}{r_1} + \frac{1}{r_2}\right)$$

where we should keep in mind that there is only *one* set of coordinates here, \mathbf{r} , for *one* particle; the r_1 and r_2 are functions of \mathbf{r} , giving the distances to nuclei 1 and 2.

We can guess that for distances close to either proton the wave function is *something like* the hydrogenic wave function

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

centered on that proton so a first guess for a trial wave function is a (normalized) sum of two such functions:

$$\psi = A[\psi_0(r_1) + \psi_0(r_2)] \quad (2.1)$$

Though such a function (a linear combination of atomic orbitals, LCAO) is simple in concept, analytically it is a bit messy. If we define the integral

$$I \equiv \langle \psi_0(r_1) | \psi_0(r_2) \rangle = \frac{1}{\pi a^3} \int e^{-(r_1+r_2)/a} d^3\mathbf{r}$$

then we can show that the normalization constant A is given by

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

We use the wave function in 2.1 to evaluate $\langle H \rangle$, we find that it is:

$$\langle H \rangle = E_1 - 2A^2 \left(\frac{e^2}{4\pi\epsilon_0} \right) \left[\langle \psi_0(r_1) | \frac{1}{r_2} | \psi(r_1) \rangle + \langle \psi_0(r_1) | \frac{1}{r_1} | \psi(r_2) \rangle \right]$$

Then if we make the definitions of the **direct** and **exchange** integrals:

$$D \equiv a \left\langle \psi_0(r_1) \left| \frac{1}{r_2} \right| \psi(r_1) \right\rangle \quad X \equiv a \left\langle \psi_0(r_1) \left| \frac{1}{r_1} \right| \psi(r_1) \right\rangle$$

These can be evaluated exactly,

$$D = \frac{a}{R} - \left(1 + \frac{a}{R}\right) e^{-2R/a} \quad X = \left(1 + \frac{r}{a}\right) e^{-R/a}$$

and used in

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

to get an estimate (i.e. upper bound) for the *electron's* energy. This does not include the potential from the proton–proton repulsion,

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

which we have to add in to get an estimate of the *total* energy of the system.

When we figure the total energy and find the value of R which minimizes it we get an equilibrium separation of

$$R = 2.4a = 1.3 \text{ \AA}$$

(compared to the experimental value of 1.06 Å) and a binding energy of 1.8 eV, as compared with an experimental value of 2.8 eV.

Chapter 3

The WKB Approximation

3.1 Generalities

The WKB method is a way of getting approximate solutions to the TISE in one dimension. It is most famously used in finding the rate of tunneling through potential barriers.

$$p(x) \equiv \sqrt{2m[E - V(x)]} \quad (3.1)$$

$$\psi(x) \approx \frac{C}{p(x)} e^{\pm \frac{i}{\hbar} \int p(x) dx} \quad (3.2)$$

3.2 Tunneling

$$\psi(x) \approx \frac{C}{\sqrt{|p(x)|}} e^{\pm \frac{1}{\hbar} \int |p(x)| dx} \quad (3.3)$$

$$T \approx e^{-2\gamma} \quad \text{where} \quad \gamma \equiv \frac{1}{\hbar} \int_0^a |p(x)| dx \quad (3.4)$$

3.2.1 Gamow Theory of α decay

We say that the alpha particle is (temporarily) trapped in a potential given by

$$V(r) = \begin{cases} -V_0 & r < r_1 \\ \frac{1}{4\pi\epsilon_0} \frac{2Ze^2}{r} & r > r_1 \end{cases} \quad (3.5)$$

The energy of the alpha particle (inside this “nucleus”) is positive and gives an outer turning point r_2 by:

$$E = \frac{1}{4\pi\epsilon_0} \frac{2Ze^2}{r_2}$$

Chapter 4

Time–Dependent Perturbation Theory

4.1 Generalities

The approximation methods of the last few sections were for the calculation of *stationary states*. As such, they are good for finding states for which we are making energy measurements but they cannot give the evolution in time of a quantum system. For processes which involve the absorption and emission of radiation one must have a theoretical handle on the solution of the *time–dependent* Schrödinger equation. In this formalism there is a basic time–independent Hamiltonian H^0 to which is added a small time–dependent piece, $H'(t)$, so that

$$H = H^0 + H'(t) \quad \text{so that} \quad H\psi = i\hbar \frac{\partial \psi}{\partial t}$$

To make things especially simple we will suppose that for the unperturbed Hamiltonian H^0 there are only two quantum levels a b , with energies E_a and E_b with orthonormal wave functions; thus

$$H^0\psi_a = E_a\psi_a \quad H^0\psi_b = E_b\psi_b \quad \langle \psi_a | \psi_b \rangle = \delta_{ab}$$

The initial state of the system is some linear combination of the two:

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

which in the absence of any perturbing $H'(t)$ would evolve according to

$$\Psi(t) = c_a\psi_a e^{-iE_a t/\hbar} + c_b\psi_b e^{-iE_b t/\hbar} \quad \text{where} \quad |c_a|^2 + |c_b|^2 = 1$$

Now consider a system where a (small) time-dependent perturbation $H'(t)$ is turned on. The state of the system $\Psi(t)$ can still be expressed as a linear combination of ψ_a and ψ_b because they form a complete set but now the coefficients c_a and c_b are functions of time:

$$\Psi(t) = c_a(t)\psi_a e^{-iE_a t/\hbar} + c_b(t)\psi_b e^{-iE_b t/\hbar} \quad (4.1)$$

Our task is now to find $c_a(t)$ and $c_b(t)$.

One can show that when the solution of the form in Eq. 4.1 is put into the time–dependent Schrödinger equation and if the diagonal matrix elements of H' vanish:

$$H'_{aa} = H'_{bb} = 0 \quad \text{where} \quad H'_{ij} \equiv \langle \psi_i | H' | \psi_j \rangle$$

then we get

$$\dot{c}_a = -\frac{i}{\hbar} H'_{ab} e^{-i\omega_0 t} c_b \quad \dot{c}_b = -\frac{i}{\hbar} H'_{ba} e^{i\omega_0 t} c_a \quad \text{where} \quad \omega_0 \equiv \frac{E_b - E_a}{\hbar} \quad (4.2)$$

which are exact.

Now suppose the system starts in the lower state:

$$c_a(0) = 1, \quad c_b(0) = 0$$

then one can show that to second order we get

$$c_b^{(1)}(t) = -\frac{i}{\hbar} \int_0^t H'_{ba}(t') e^{i\omega_0 t'} dt' \quad (4.3)$$

For the special case that the time dependence of the perturbation is sinusoidal:

$$H'(\mathbf{r}, t) = V(\mathbf{r}) \cos(\omega t)$$

so that

$$H'_{ab} = V_{ab} \cos(\omega t) \quad \text{where} \quad V_{ab} \equiv \langle \psi_a | V | \psi_b \rangle.$$

From this and Eq. 4.3 we can show that the **transition probability**, i.e. the probability that the particle starting off in state a will be found at time t in state b is

$$P_{a \rightarrow b} = |c_b(t)|^2 \approx \frac{|V_{ab}|^2}{\hbar^2} \frac{\sin^2[(\omega_0 - \omega)t/2]}{(\omega_0 - \omega)^2} \quad (4.4)$$

This result used the assumption

$$\omega_0 + \omega \gg |\omega_0 - \omega|$$

That is, the driving frequency ω is very close to the transition frequency ω_0 .

4.2 Emission and Absorption of Radiation

We now consider the case where the perturbing Hamiltonian comes from the (sinusoidally-varying) electric field of an electromagnetic wave. We consider the effect on an atom, on which the effect of the magnetic field component of the wave is small. For a wave polarized in the z direction (and propagating, say along the $+y$ direction) the oscillating field is

$$\mathbf{E} = E_0 \cos(\omega t) \hat{\mathbf{z}}$$

so that for a charge q contained in the atom the perturbing Hamiltonian is

$$H' = -qE_0 z \cos(\omega t)$$

for which

$$H'_{ba} = -\mathbf{p} E_0 \cos(\omega t) \quad \text{where} \quad \mathbf{p} \equiv q \langle \psi_b | z | \psi_a \rangle \quad (4.5)$$

This perturbation, which is odd in z and the states we will consider are either even or odd in z but in both cases the diagonal matrix elements of H' will vanish. Thus we can use our result for the oscillatory perturbation with

$$V_{ba} = -\mathbf{p} E_0$$

We find that the transition probability (for a particle of charge q in our “atom” making the transition from state ψ_a to state ψ_b) is

$$P_{a \rightarrow b}(t) = \left(\frac{|\mathbf{p}| E_0}{\hbar} \right)^2 \frac{\sin^2[(\omega_0 - \omega)t/2]}{(\omega_0 - \omega)^2} \quad (4.6)$$

We also find for a system starting in the *upper* state (so that $c_a(0) = 0$ and $c_b(0) = 1$),

$$P_{b \rightarrow a}(t) = \left(\frac{|\mathbf{p}| E_0}{\hbar} \right)^2 \frac{\sin^2[(\omega_0 - \omega)t/2]}{(\omega_0 - \omega)^2} \quad (4.7)$$

which is a surprising result; a particle in the upper state can make a transition to the *lower* state under the influence of the external field, and the probability for the transition is exactly the same. The latter phenomenon is known as **stimulated emission** and is behind the working of lasers.

Another mechanism by which an atom can “de-excite” is *spontaneous emission*, which occurs in the absence of an external field. The full reasons require a study of the quantization of the EM field, which will have to wait for grad school. But shortly, we will derive the rate for spontaneous emission by exploiting a connection with thermodynamics and a result you already know (?) for thermal radiation.

The above expressions apply to a monochromatic wave of a single direction of propagation and polarization, where the amplitude E_0 is given. One would like to have a result for stimulated emission which can be used when the radiation has a range of frequencies and is averaged over all incident directions and polarizations. (We also want to work with the *energy density* of the EM wave.)

After some careful integrations over directions and using the expression for the energy density of electromagnetic wave,

$$u = \frac{\epsilon_0}{2} E_0^2$$

one can show: The transition rate for stimulated emission from state b to state a under the influence of incoherent, unpolarized light incident from all directions is

$$R_{b \rightarrow a} = \frac{\pi}{3\epsilon_0 \hbar^2} |\mathbf{p}|^2 \rho(\omega_0) \quad \text{where} \quad \mathbf{p} \equiv q \langle \psi_b | \mathbf{r} | \psi_a \rangle \quad (4.8)$$

and where $\rho(\omega_0)$ is the energy density in the fields per unit frequency, evaluated at ω_0 .

4.3 Spontaneous Emission

The key to deriving the spontaneous emission rate is an empirical theory developed by Einstein before quantum mechanics even existed. He argued that the rate of change in the numbers of atoms in the upper state ψ_b is related to the numbers of atoms in the upper and lower states (N_b and N_a , respectively) by

$$\frac{dN_b}{dt} = -N_b A - N_b B_{ba} \rho(\omega_0) + N_a B_{ab} \rho(\omega_0) \quad (4.9)$$

Here the B ’s are related to the *induced* emission and absorption coefficients hence they must be multiplied by the energy density to get a rate. The A is from spontaneous emission and does not

need the energy density factor. At thermal equilibrium, using $dN_b/dt = 0$ and the Boltzmann factor from basic stat mech, one can show:

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

which we compare to the Planck blackbody formula for the energy density of radiation which is in equilibrium with a body of temperature T (also from stat mech):

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

and comparison of the two expressions from ρ gives

$$B_{ab} = B_{ba} \quad \text{and} \quad A = \frac{\omega_0^3 \hbar}{\pi^2 c^3} B_{ba}$$

and using our previous result for the rate of induce emission we find

$$B_{ba} = \frac{\pi}{3\epsilon_0 \hbar^2} |\mathbf{p}|^2$$

and finally

$$A = \frac{\omega_0^3 |\mathbf{p}|^2}{3\pi\epsilon_0 \hbar c^3} \quad (4.10)$$

4.3.1 Lifetime of an Excited State

Spontaneous emission (by itself) gives a change in the number of atoms in state b proportional to the number of atoms still in that state and the time interval dt :

$$dN_b = -AN_b dt$$

from which we get the exponential decay law

$$N_b(t) = N_b(0)e^{-At} \quad (4.11)$$

with the lifetime τ defined by

$$\tau = \frac{1}{A} \quad \text{so that} \quad N_b(t) = N_b(0)e^{-t/\tau}$$

An H atom in the $n = 2, l = 1$ states can decay to the ground state. When we do the calculation (Problem 9.11) we find a lifetime of 1.60×10^{-9} s.

4.3.2 Selection Rules

Since for the (first-order!) emission rates have depended on the matrix elements

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

it is very useful to know when these are *zero*; for the H atom, these come down to evaluating

$$\langle n' l' m' | \mathbf{r} | n l m \rangle$$

and we can use the properties of the angular momentum eigenstates to tell when these vanish.

One can show that for the relatively simple system of the H atom, no transitions occur unless

$$\Delta l = \pm 1 \quad \text{and} \quad \Delta m = \pm 1 \quad \text{or} \quad 0$$

Chapter 5

Scattering Theory

Note: This section could use a lot of good illustrations to clarify geometries of the definitions and examples. Someday I'll draw them; for now look at the ones in the book!

5.1 Generalities

Scattering theory (or **collision theory**) is the study of the motion of two or more particles which move freely for a long time, have a brief interaction and then (in the same internal states or else changed somewhat) move freely once again. It can be treated with classical mechanics or with quantum mechanics, but since the main use of the theory is to study the interactions of particles on the atomic scale, we nearly always hear about the quantum theory of scattering.

The collision described above is a *special type* of quantum motion of course, but it is of enormous importance for the analysis of experiments where we have little choice but to carry out such collisions. Because of this, the basic quantities and methods of calculation that make up collision theory are of enormous importance in physics research.

5.2 Classical Scattering

We consider a fixed scattering center and an incident particle of mass with kinetic energy E . The particle comes in at a distance b (measured perpendicularly to the main axis; see the figures in the book until I draw my own here!). The particle emerges and at large distances is moving at some angle θ from its original motion. The distance b is the **impact parameter** and the angle θ is the **scattering angle**. The main problem of classical scattering theory is: given E and b , find the scattering angle θ .

More generally the particles that approach the target within some small cross-sectional area $d\sigma$ will exit within a small solid angle $d\Omega$. At a given spherical angle θ (we will take the scattering process to be independent of ϕ), the proportionality factor between the two is $D(\theta)$, also denoted by $\frac{d\sigma}{d\Omega}$:

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

Substituting $d\sigma = b db d\phi$ and $d\Omega = \sin \theta d\theta d\phi$, this gives

$$D(\theta) = \frac{d\sigma}{d\Omega} = \frac{b}{\sin \theta} \left| \frac{db}{d\theta} \right| \quad (5.1)$$

$D(\theta)$ is known as the **differential cross section**

Note that $D(\theta)$ has units of area (e.g. m^2) but to remind ourselves of the solid angle that goes into the definition we often give it as an area *per steradian*.

The **total cross section** is defined by

$$\sigma \equiv \int D(\theta) d\Omega$$

which, very loosely, gives the total area of the incoming beam which is scattered by the target.

In terms of experimental quantities, if the beam luminosity \mathcal{L} is defined by

$$\mathcal{L} \equiv \text{number of incident particles per area, per time}$$

and the number of particles scattered into solid angle $d\Omega$ per unit time is dN , then using the fact that $\mathcal{L} d\sigma = N d\Omega$, one can show:

$$D(\theta) = \frac{d\sigma}{d\Omega} = \frac{1}{\mathcal{L}} \frac{dN}{d\Omega} \quad (5.2)$$

5.2.1 Examples

While one can study any central potential $V(r)$ to get the relation between b and θ , we look at two which have simple and/or interesting results.

For the “hard sphere” potential (basically, $V = 0$ for $r > R$ and $V = \infty$ for $r < R$) geometry gives the result:

$$\theta = \begin{cases} 2 \cos^{-1}(b/R) & b \leq R \\ 0 & b \geq R \end{cases}$$

which gives differential and total cross sections of:

$$D(\theta) = \frac{R^2}{4} \quad \sigma = \pi R^2$$

An example of greater physical importance is the Coulomb potential, where we suppose for simplicity one of the charged particles is very massive and serves as the target. The potential is

$$V(r) = \frac{1}{4\pi\epsilon_0} \frac{q_1 q_2}{r}$$

The problem of orbits in an inverse-square force is solved in every quality mechanics text; we’re considering the case of an unbound particle (i.e. the projectile) and it will have a hyperbolic orbit. One can adapt that result to geometry considered here (that is, an impact parameter b and an outgoing angle θ) and one finds that if the projectile’s kinetic energy is E , then

$$b = \left(\frac{q_1 q_2}{8\pi\epsilon_0 E} \right) \cot \frac{\theta}{2}$$

which gives

$$D(\theta) = \left[\frac{q_1 q_2}{16\pi\epsilon_0 E \sin^2(\theta/2)} \right]^2 \quad (5.3)$$

but when we use this to calculate the total cross section σ we get an infinite result! Loosely, one says that for a scattering process you can’t escape from the Coulomb potential; *all* particles are scattered. It is also expressed by saying that the Coulomb potential is “long-ranged”.

This is first of many mathematical problems that are encountered with this very important potential. For scattering of (say) alpha particles on a nucleus, while a few particles may get to feel the potential from the short-ranged nuclear force, the great majority feel only the Coulomb force, so it is essential to deal with it somehow. Of course in a real target the atomic electrons completely screen the nuclei but that is only at very large distances in comparison with nuclear sizes. All that comes up later (maybe) in the applications.

5.3 Quantum Scattering Theory

As the atomic world works via quantum mechanics and *not* classical mechanics we need to formulate the theory of scattering using the concepts and language of quantum mechanics. From the start we see that even though it makes sense to talk about the measurement of a particle's final direction of motion as lying within some solid angle $d\Omega$, speaking about a definite impact parameter b makes even less sense than for a hypothetical experiment in a classical setting.

For this reason, we can still use the experimental definition of the differential cross section in Eq. 5.2 but we need to find how it relates to quantities relevant for quantum mechanics.

Considering how a scattering must be described in the QM picture, it would seem extremely difficult to solve. A normalized *wave packet* for the incoming particle moves toward the scattering center; this is a *time-dependent* wave function! After the interaction there is a (normalized) wave going outward in all directions giving the probability of measuring the particle's final momentum along some spherical direction. This would seem to be an extremely hard problem to solve for *any* potential $V(r)$. In practice, if one can make an initial leap of faith to accept a very reasonable and simple (though rigorously shady) form for the wave function of the scattered particle, the analysis is *relatively* simple.

The form for the wave function applies at large r , where it takes the form of a plane wave propagating in the $+z$ direction summed with an outward-going spherical wave, all multiplied by some unknown constant. This general form is:

$$\psi(r, \theta) \approx A \left\{ e^{ikz} + f(\theta) \frac{e^{ikr}}{r} \right\} \quad (5.4)$$

In Eq. 5.4, k has the usual relation with the kinetic energy of the particle,

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

and again, for the record, we are assuming azimuthal (ϕ) symmetry for the state of the target particle and hence for the scattering process.

One can show:

$$D(\theta) = \frac{d\sigma}{d\Omega} = |f(\theta)|^2 \quad (5.5)$$

5.4 Partial Wave Analysis

Since the potential is central we know from dealing with the Schrödinger equation in spherical coordinates that the equation separates into radial and angular parts. Then the solution is a sum of terms of the form

$$\psi(r, \theta, \phi) = R_l(r) Y_l^m(\theta, \phi)$$

We make the common substitution $u_l(r) \equiv rR_l(r)$, and then the radial equation for each u_l is

$$-\frac{\hbar^2}{2m} \frac{d^2 u_l}{dr^2} + \left[V(r) + \frac{\hbar^2}{2m} \frac{l(l+1)}{r^2} \right] u_l = E u_l \quad (5.6)$$

and when we can solve this for each l , we have the solution for ψ . We will then have to relate the answer to $f(\theta)$. Note, from the boundary conditions and the fact that we have *imposed* the value of the energy from the beginning, there will be *one* solution for the radial function $u_l(r)$.

We will assume that the potential $V(r)$ is short-ranged, than is, is goes to zero at large r at least as fast as the centrifugal term in Eq. 5.6. The Coulomb potential does *not* satisfy this and it requires special treatment.

At large r then, we can ignore both the centrifugal term *and* $V(r)$ and then 5.6 gives

$$\frac{d^2 u_l}{dr^2} \approx -k^2 u_l$$

which has the solution

$$u_l(r) = C e^{ikr} + D e^{-ikr}$$

but for the region where we can ignore the scattering potential but not the centrifugal potential the radial equation is

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

which as we saw earlier in Chapter 4 has the general solution

$$u_l(r) = A j_l(kr) + B n_l(kr) .$$

In Chapter 4 we ignore the $n_l(kr)$ functions since they blow up at $r = 0$ but here we have to include them since we are finding the solution in a region which does *not* include $r = 0$.

Actually we don't really want *either* the j_l or the n_l functions since we are interested in solutions which goes like e^{ikr}/r at large r which if nothing else is *complex*; we need some combination of the j_l and n_l . The combinations we want to consider are

$$h_l^{(1)}(x) \equiv j_l(x) + i n_l(x) \quad \text{which at large } x \text{ goes like } \frac{e^{ix}}{x}$$

and

$$h_l^{(2)}(x) \equiv j_l(x) - i n_l(x) \quad \text{which at large } x \text{ goes like } \frac{e^{-ix}}{x}$$

These combinations are known as **spherical Hankel functions**. At large r , the radial function $R_l(r)$ must “go like” $h_l^{(1)}(kr)$. Then outside the scattering region (where $V(r)$ is negligible) the wave function is

$$\psi(r, \theta, \phi) = A \left\{ e^{ikz} + \sum_{l,m} C_{l,m} h_l^{(1)}(kr) Y_l^m(\theta, \phi) \right\}$$

We assume the potential is spherically symmetric and then the wave function can only depend on θ . Because of this we can only have terms with $m = 0$, and using

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

we get

$$\psi(r, \theta) = A \left\{ e^{ikz} + k \sum_l^{\infty} i^{l+1} (2l+1) a_l h_l^{(1)}(kr) P_l(\theta) \right\} \quad (5.7)$$

The (complex) numbers a_l are called the **partial wave amplitudes**.

From this we can already pick off the expression for the scattering amplitude:

$$\psi(r, \theta) \approx A \left\{ e^{ikz} + f(\theta) \frac{e^{ikr}}{r} \right\} \implies f(\theta) = \sum_{l=0}^{\infty} (2l+1) a_l P_l(\cos \theta)$$

and from this it can be shown that the total cross section is

$$\sigma = 4\pi \sum_{l=0}^{\infty} (2l+1) |a_l|^2 P_l^2(\cos \theta)$$

To actually *find* the a_l 's we need to *solve* the Schrödinger equation and find its behavior at large r . To do that we need to include the plane wave e^{ikz} in Eq. 5.7 with the other sum. For this, we use the expansion

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

to get

$$\psi(r, \theta) = A \sum_{l=0}^{\infty} i^l (2l+1) \left[j_l(kr) + i k a_l h_l^{(1)}(kr) \right] P_l(\cos \theta) \quad (5.8)$$

And in principle at least we can see how to find a_l . Take the *full* radial equation for each $R_l(kr)$ (*including* the short-ranged potential) and, starting from the origin integrate it up to large value of r and then out in these nether regions express it as a linear combination of $j_l(kr)$ and $h_l^{(1)}(kr)$. The “normalization” of this $R_l(kr)$ doesn't matter since one can pull a_l off the *ratio* of the coefficients.

Then, once we have the a_l 's, calculate $f(\theta)$ and confer with the experimenters.

5.4.1 Phase Shifts

While the information for a scattering process (at a given energy) *could* be expressed in terms of the a_l 's, there is a more common representation known as partial wave **phase shifts**.

By analogy with one-dimensional scattering (see discussion in text) the partial wave $\psi^{(l)}$ can be said to pick up a phase shift relative to the wave one measures for the zero-potential case. This means that whereas for $V = 0$ $\psi^{(l)}$ has the large- r form

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

with a scattering potential in place the outgoing part picks a phase shift δ_l :

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

where the factor of 2 that goes with δ_l is by the convention that there is a phase shift of the wave on the way *in* and on the way *out* from the scattering center.

Equating the asymptotic forms for $\psi^{(l)}$ gives the relation between a_l and δ_l :

$$a_l = \frac{1}{2ik} \left(e^{2i\delta_l} - 1 \right) = \frac{1}{k} e^{i\delta_l} \sin(\delta_l) \quad (5.9)$$

And the scattering amplitude and total cross section has fairly simple expressions in terms of the phase shifts:

$$f(\theta) = \frac{1}{k} \sum_{l=0}^{\infty} (2l+1) e^{i\delta_l} \sin(\delta_l) P_l(\cos \theta) \quad (5.10)$$

and

$$\sigma = \frac{4\pi}{k^2} \sum_{l=0}^{\infty} (2l+1) \sin^2(\delta_l) \quad (5.11)$$

5.5 The Born Approximation

Since for a simple (close-ranged) potential of the form $V(r)$ one can always do a numerical integration out beyond the scattering potential and thus find the phase shifts “exactly”, one could ask why we need to think about any approximation methods at all. But there are reasons to study approximations in scattering theory: along the way we will learn the important mathematical technique of “Green functions”; we will develop a series solution for scattering which can in principle be computed to arbitrary accuracy; and the lowest-order approximations for scattering will yield some simple and interesting analytic expressions.

5.5.1 Integral Form of the Schrödinger Equation

The time-independent Schrödinger equation is

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

which can be written

$$(\nabla^2 + k^2)\psi = Q \quad (5.12)$$

where

$$k \equiv \frac{\sqrt{2mE}}{\hbar} \quad \text{and} \quad Q \equiv \frac{2m}{\hbar^2} V\psi$$

Now, we are trying to *solve for* ψ and ψ actually appears inside Q ; we can’t forget that, but for the moment we will pretend that Q is some *given* function and study the technique of solving differential equations using **Green functions**.

5.5.2 Green Functions

We review from basic results from electrostatics but expressed in a new way.

From the Maxwell equations (and the relation $\mathbf{E} = -\nabla V$) we get:

$$\nabla^2 V = \nabla \cdot (\nabla V) = -\nabla \cdot \mathbf{E} = -\frac{\rho}{\epsilon_0} \quad \implies \quad \nabla^2 V = -\frac{\rho}{\epsilon_0}$$

We also know that we can get the potential from a localized charge distribution using

$$V(\mathbf{r}) = \frac{1}{4\pi\epsilon_0} \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}'$$

Now we can start with the second of these relations and show that the first follows from it but is there a way to *start* from the first relation and arrive at the second?

We will begin with $\nabla^2 V = -\rho/\epsilon_0$. Suppose we can solve the differential equation

$$\nabla^2 G(\mathbf{r}) = \delta^3(\mathbf{r}) \quad (5.13)$$

Such a solution will also give (with ∇ meaning differentiation with respect to unprimed coordinates),

$$\nabla^2 G(\mathbf{r} - \mathbf{r}') = \delta^3(\mathbf{r} - \mathbf{r}')$$

If we had such a solution then we can use it to *invert* the differential equation for V ;

$$V(\mathbf{r}) = \int G(\mathbf{r} - \mathbf{r}') \left(-\frac{\rho(\mathbf{r}')}{\epsilon_0} \right) d^3\mathbf{r}'$$

This expression comes from taking the Green function, multiplying the right side of the original DE and then integrating. So that's the *procedure*, but we should show that this *is* a solution:

$$\begin{aligned} \nabla^2 V &= \nabla^2 \int G(\mathbf{r} - \mathbf{r}') \left(-\frac{\rho(\mathbf{r}')}{\epsilon_0} \right) d^3\mathbf{r}' \\ &= \int \nabla^2 G(\mathbf{r} - \mathbf{r}') \left(-\frac{\rho(\mathbf{r}')}{\epsilon_0} \right) d^3\mathbf{r}' = \int \delta^3(\mathbf{r} - \mathbf{r}') \left(-\frac{\rho(\mathbf{r}')}{\epsilon_0} \right) d^3\mathbf{r}' \\ &= -\frac{\rho(\mathbf{r})}{\epsilon_0} \end{aligned}$$

So what is this function $G(\mathbf{r})$ which has the property in Eq. 5.13? It happens to be

$$G(\mathbf{r}) = -\frac{1}{4\pi} \frac{1}{r} \quad \implies \quad G(\mathbf{r} - \mathbf{r}') = -\frac{1}{4\pi} \frac{1}{|\mathbf{r} - \mathbf{r}'|}$$

as we know from the first chapter of Griffiths' EM book. With this *explicit* expression for the Green function, we have

$$V(\mathbf{r}) = -\frac{1}{4\pi} \int \frac{1}{|\mathbf{r} - \mathbf{r}'|} \left(-\frac{\rho(\mathbf{r}')}{\epsilon_0} \right) d^3\mathbf{r}' = \frac{1}{4\pi\epsilon_0} \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}'$$

and in this way the integral expression *follows from* the differential equation.

It's not really this simple... we've been careless about boundary conditions on $V(\mathbf{r})$ and on the uniqueness of the solution we found for $G(\mathbf{r})$, but it's really the *method* we're after and you can exercise greater in a more advanced course in theoretical physics.

5.5.3 Back to the Schrödinger equation

Now go back to Eq. 5.12. We see from our experience with the Poisson equation that we now want to find a Green function $G(\mathbf{r})$ satisfying

$$(\nabla^2 + k^2)G(\mathbf{r}) = \delta^3(\mathbf{r}) \quad (5.14)$$

If we succeed in finding such a function then from Eq. 5.12 we expect that a solution for ψ will be given (more or less) by

$$\psi(\mathbf{r}) = \int G(\mathbf{r} - \mathbf{r}') Q(\mathbf{r}') d^3\mathbf{r}' . \quad (5.15)$$

Finding this $G(\mathbf{r})$ will take some work (unlike the Green function for the Poisson equation, where the result was already known). A more complete derivation (will a few cut corners) can be found in the text, but the gist of it is like this:

First, we'll work with the Fourier transform of G , which we'll call $g(\mathbf{s})$, where

$$G(\mathbf{r}) = \frac{1}{(2\pi)^{3/2}} \int e^{i\mathbf{s}\cdot\mathbf{r}} g(\mathbf{s}) d^3\mathbf{s} \quad (5.16)$$

From the condition on G and the use of an integral expression for the delta function, one gets:

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

so with this explicit form for g we just put it back into Eq. 5.16:

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

but in fact this integral is not so easy and there are problems (or at least *ambiguities*) to be dealt with because of the behavior of the integrand at points where $s = k$.

After much work, some of it involving integrals over paths in the complex plane (see the Phys 2920 notes by your truly) one arrives at

$$G(\mathbf{r}) = -\frac{e^{ikr}}{4\pi r} \quad (5.17)$$

So putting this back into Eq. 5.15, it would seem that we get

$$\psi(\mathbf{r}) = -\frac{1}{4\pi} \int \frac{e^{ik|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|} Q(\mathbf{r}') d^3\mathbf{r}' . \quad (5.18)$$

and we do... well, almost. First, this is a solution to the inhomogeneous equation Eq. 5.12 and so we can add to it the solution to the homogeneous equation. The homogeneous equation,

$$(\nabla^2 + k^2)\psi_0 = 0$$

is the one where the potential V is zero, and the incoming plane wave is a solution to that. Thus, to 5.18 we need to add the incoming plane wave which we denote as $\psi_0(\mathbf{r})$.

Secondly, we must recall that Q itself depends on ψ ; recall that $Q \equiv (2m/\hbar^2)V\psi$. Putting all of this into 5.18 gives

$$\psi(\mathbf{r}) = \psi_0(\mathbf{r}) - \frac{m}{2\pi\hbar^2} \int \frac{e^{ik|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|} V(\mathbf{r}') \psi(\mathbf{r}') d^3\mathbf{r}' . \quad (5.19)$$

which we will take to be the **integral form of the Schrödinger equation**. Of course, it is *not* an explicit solution because $\psi(\mathbf{r})$ also appears inside the integral on the right hand side. But in this form we can get approximate solutions in a systematic way.

5.5.4 The First Born Approximation

Before introducing any physical approximations, we perform a *mathematical* approximation which depends only on the potential being short-ranged, such that we can approximate $|\mathbf{r}| \gg |\mathbf{r}'|$ for any \mathbf{r}' likely to contribute to the integral in 5.19. We are justified in making the replacement

$$\frac{e^{ik|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|} \approx \frac{e^{ikr}}{r} e^{-i\mathbf{k}\cdot\mathbf{r}'}$$

where $\mathbf{k} \equiv k\hat{\mathbf{r}}$ and we also want

$$\psi_0(\mathbf{r}) = Ae^{ikr}$$

From this expression we can extract the scattering amplitude (it is the part apart from the plane wave multiplying e^{ikr}/r) and one finds

$$f(\theta, \phi) = -\frac{m}{2\pi\hbar^2 A} \int e^{-i\mathbf{k}\cdot\mathbf{r}'} V(\mathbf{r}') \psi(\mathbf{r}') d^3\mathbf{r}'$$

which we can take to be *exact* and is also quite unusable because we don't know $\psi(\mathbf{r})$.

Now we make the approximation that the incoming plane wave is not altered much by the scattering potential. This implies that inside the integral we can use:

$$\psi(\mathbf{r}') \approx \psi_0(\mathbf{r}') = Ae^{ikz'} = Ae^{i\mathbf{k}\cdot\mathbf{r}'}$$

where $\mathbf{k} = k\hat{\mathbf{z}}$. With this, we get the (first) **Born approximation** for the scattering amplitude,

$$f(\theta, \phi) \approx -\frac{m}{2\pi\hbar^2} \int e^{i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{r}'} V(\mathbf{r}') d^3\mathbf{r}' \quad (5.20)$$

We note that with the definition of $\boldsymbol{\kappa}$ as the **momentum transfer** for the collision:

$$\boldsymbol{\kappa} \equiv \mathbf{k}' - \mathbf{k}$$

then the Born approximation relates the scattering amplitude to the Fourier transform of the potential $V(\mathbf{r})$.

There are two interesting special cases which simplify 5.20 even further. The first is for **low energy scattering**, where the wavelength of the incident particle is much larger than the extent of the potential. It gives:

$$f(\theta, \phi) \approx -\frac{m}{2\pi\hbar^2} \int V(\mathbf{r}) d^3\mathbf{r} \quad (\text{low energy!}) \quad (5.21)$$

The other special case is the common one where the potential is spherically symmetric, that is, $V(\mathbf{r}) = V(r)$. Then one can show

$$f(\theta) \approx -\frac{2m}{\hbar^2 \kappa} \int_0^\infty r V(r) \sin(\kappa r) dr \quad (5.22)$$

where κ , the magnitude of the momentum transfer is

$$\kappa = 2k \sin(\theta/2)$$

Griffiths works two important examples using the first Born approximation. If we consider the **Yukawa potential**

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

then we get an approximate scattering amplitude

$$f(\theta) \approx -\frac{2m\beta}{\hbar^2} (\mu^2 + \kappa^2)$$

We might then get the clever idea that we can get the answer for the *Coulomb* potential from the result for the *Yukawa* potential by replacing β and letting μ go to zero:

$$\beta = \frac{q_1 q_2}{4\pi\epsilon_0} \quad \text{and} \quad \mu \longrightarrow 0$$

When we do this, we get

$$f(\theta) \approx \frac{q_1 q_2}{16\pi\epsilon_0 E \sin^2(\theta/2)} \quad \Longrightarrow \quad \frac{d\sigma}{d\Omega} = |f(\theta)|^2 = \left[\frac{q_1 q_2}{16\pi\epsilon_0 E \sin^2(\theta/2)} \right]^2$$

which in fact is the same as the *classical* formula used by Rutherford, Eq. 5.3. and it is known from a direct but *rigorous* solution for the Coulomb potential that this is correct, but we must regard this limit for the Yukawa potential as a lucky accident because in our analysis we were *excluding* the Coulomb potential. So the correct treatment requires more work; in fact it requires us to go back and re-examine the asymptotic solutions for R_l . Wait for graduate school.

The fact that the *correct* treatment of Coulomb gives the *classical* result is another lucky and ironic accident. As Rutherford deduced the structure of the atom using the classical formula, giving rise to the theoretical studies which gave us quantum mechanics it was always possible that the correct formula for $\frac{d\sigma}{d\Omega}$ would be different and that Rutherford would have come to the right conclusion about the atom for the wrong reason. But in the end his formula *was* correct and Rutherford has the last laugh¹.

5.5.5 The Born Series

We repeat Eq. 5.19 in a slightly cleaner form:

$$\psi(\mathbf{r}) = \psi_0(\mathbf{r}) + \int g(\mathbf{r} - \mathbf{r}') V(\mathbf{r}') \psi(\mathbf{r}') d^3\mathbf{r}' \quad (5.23)$$

where

$$\psi_0(\mathbf{r}) = A e^{i\mathbf{k} \cdot \mathbf{r}} \quad \text{and} \quad g(\mathbf{r}) \equiv -\frac{m}{2\pi\hbar^2} \frac{e^{ikr}}{r}$$

Writing it even more compactly (at the cost of not making the coordinate dependences clear) this is

$$\psi = \psi_0 + \int gV\psi \quad (5.24)$$

If we buy this equation, it is certainly the case that we can take the ψ on the left side and recycle it into the right side. Again suppressing the variable dependences, this would give

$$\psi = \psi_0 + \int gV\psi_0 + \int \int gVgV\psi \quad (5.25)$$

Clearly, repeated recycling of the left side gives an infinite series:

$$\psi = \psi_0 + \int gV\psi_0 + \int \int gVgV\psi_0 + \int \int \int gVgVgV\psi_0 + \dots \quad (5.26)$$

where one would hope that the successive terms get smaller so that it makes any sense. The g function is often called a **propagator** and the factor of the potential V might be called a **vertex factor**.

This series can be represented with pictures (see the text) and as such has a lot in common with the little pictures known as **Feynman diagrams**. Both are a systematic way of calculating a scattering amplitude, but the Feynman diagrams come from a full relativistic theory which permits the creation and destruction of particles, so there is only a *similarity* in these calculations.

¹A very loud laugh if we believe the stories about Rutherford.