

Physics 221B
Spring 2011
Notes 32
Time-Dependent Perturbation Theory

1. Introduction

Time-dependent perturbation theory applies to Hamiltonians of the form

$$H = H_0 + H_1(t), \tag{1}$$

where H_0 is solvable and H_1 is treated as a perturbation. In bound state perturbation theory (see Notes 21) we were interested in the shifts in the energy levels and eigenfunctions of the unperturbed system induced by the perturbation H_1 , which was assumed to be time-independent. In time-dependent perturbation theory, on the other hand, we are usually interested in time-dependent transitions between eigenstates of the unperturbed system induced by the perturbation H_1 . In time-dependent perturbation theory the perturbation H_1 is allowed to depend on time, as indicated by Eq. (1), but it does not have to be time-dependent, and in fact in practice often it is not. Time-dependent perturbation theory is especially useful in scattering theory, problems involving the emission and absorption of radiation, and in field theoretic problems of various kinds. Such problems will occupy us for the rest of the course.

Time-dependent transitions are usually described by the *transition amplitude*, defined as the quantity

$$\langle f|U(t)|i\rangle, \tag{2}$$

where $U(t)$ is the exact time evolution operator for the Hamiltonian (1), and where $|i\rangle$ and $|f\rangle$ are two eigenstates of the unperturbed Hamiltonian H_0 (the “initial” and “final” states). The transition amplitude can be regarded as simply a matrix element of the exact time evolution operator in the eigenbasis of the unperturbed Hamiltonian, but it is also the amplitude to find the system in state $|f\rangle$ when it was known to be in the state $|i\rangle$ at $t = 0$. Thus, the absolute square of the transition amplitude is the *transition probability*, the probability to make the transition $i \rightarrow f$ in time t . Often we are interested in transitions to some collection of final states, in which case we must sum the transition probabilities over all these states.

In these Notes we shall develop the basic formalism of time-dependent perturbation theory and study some simple examples. For the most part we shall simply follow the formulas to see where they lead, without examining the conditions of validity or the limitations of the results. Those questions are better addressed in the context of some examples, which we shall do as we look at examples, some in these Notes and some later in the course.

2. Time-Evolution Operators

Let us denote the unperturbed time-evolution operator by $U_0(t)$ and the exact one by $U(t)$. Since the full Hamiltonian may depend on time, the exact time-evolution operator actually depends on two times, t and t_0 , but we shall set $t_0 = 0$ and just write $U(t)$. See Sec. 5.2. These operators satisfy the evolution equations,

$$i\hbar \frac{\partial U_0(t)}{\partial t} = H_0 U_0(t), \quad (3a)$$

$$i\hbar \frac{\partial U(t)}{\partial t} = H(t)U(t), \quad (3b)$$

which are versions of Eq. (5.12). Since H_0 is independent of time, Eq. (3a) can be solved,

$$U_0(t) = e^{-iH_0 t/\hbar}, \quad (4)$$

but if H_1 depends on time then there is no similarly simple expression for $U(t)$.

3. The Interaction Picture

The *interaction picture* is a picture that is particularly convenient for developing time-dependent perturbation theory. It is intermediate between the Schrödinger and Heisenberg pictures that were discussed in Sec. 5.5. Recall that in the Schrödinger picture, the kets evolve in time but the operators do not (at least if they have no explicit time dependence), while in the Heisenberg picture the kets do not evolve but the operators do. In the interaction picture, the time evolution of the kets in the Schrödinger picture that is due to the unperturbed system H_0 is stripped off, leaving only the evolution due to the perturbation H_1 . This is presumably slower than the evolution due to the whole Hamiltonian H , since H_1 is assumed small compared to H_0 . We will not attempt to state precisely what “small” means in this context, but rather we will develop the perturbation expansion as a power series in H_1 and then examine its limitations in various examples.

In the following we shall use an S subscript on kets and operators in the Schrödinger picture, and an I on those in the interaction picture. We will not use the Heisenberg picture in these Notes. If the subscript is omitted, the Schrödinger picture will be assumed. The relation between the kets in the Schrödinger and interaction pictures is

$$|\psi_I(t)\rangle = U_0^\dagger(t) |\psi_S(t)\rangle. \quad (5)$$

Compare this to Eq. (5.16), which shows the relation between kets in the Schrödinger and Heisenberg pictures. The difference is that in Eq. (5) we are only stripping off the evolution due to H_0 , not the whole time evolution. Notice that at $t = 0$ the Schrödinger and interaction picture kets agree,

$$|\psi_I(0)\rangle = |\psi_S(0)\rangle. \quad (6)$$

As for operators in the interaction picture, they are defined by

$$A_I(t) = U_0^\dagger(t) A_S(t) U_0(t). \quad (7)$$

Sometimes A_S may be time-independent, but A_I will always be time-dependent. Compare this to Eq. (5.18), which shows the relation between operators in the Schrödinger and Heisenberg pictures.

4. The Dyson Series

Let us define $W(t)$ as the operator that evolves kets in the interaction picture forward from time 0 to final time t :

$$|\psi_I(t)\rangle = W(t)|\psi_I(0)\rangle. \quad (8)$$

The operator $W(t)$ is a time-evolution operator, but we use the symbol W to avoid confusion with the two other time-evolution operators introduced so far, $U_0(t)$ and $U(t)$.

It is easy to find a relation among these three operators. Substituting Eqs. (5) and (6) into Eq. (8), we have

$$|\psi_I(t)\rangle = U_0(t)^\dagger |\psi_S(t)\rangle = U_0(t)^\dagger U(t) |\psi_S(0)\rangle = W(t) |\psi_S(0)\rangle, \quad (9)$$

or, since $|\psi_S(0)\rangle$ is arbitrary,

$$W(t) = U_0(t)^\dagger U(t). \quad (10)$$

The operator $W(t)$ is equivalent to first evolving forward for time t under the exact Hamiltonian, then evolving backwards for the same time under the unperturbed Hamiltonian.

We obtain a differential equation for $W(t)$ by differentiating Eq. (10) and using Eqs. (3),

$$\begin{aligned} i\hbar \frac{\partial W(t)}{\partial t} &= i\hbar \frac{\partial U_0(t)^\dagger}{\partial t} U(t) + U_0(t)^\dagger i\hbar \frac{\partial U(t)}{\partial t} = -U_0(t)^\dagger H_0 U(t) + U_0(t)^\dagger H U(t) \\ &= U_0(t)^\dagger H_1 U(t) = [U_0(t)^\dagger H_1 U_0(t)] [U_0(t)^\dagger U(t)], \end{aligned} \quad (11)$$

where we have used $H = H_0 + H_1$ in the third equality, whereupon the terms in H_0 cancel. The result can be written,

$$i\hbar \frac{\partial W(t)}{\partial t} = H_{1I}(t) W(t), \quad (12)$$

an equation of the same form as Eqs. (3), but one in which only the perturbing Hamiltonian H_1 appears, and that in the interaction picture. By applying both sides of Eq. (12) to the initial state $|\psi_I(0)\rangle$, we obtain a version of the Schrödinger equation in the interaction picture,

$$i\hbar \frac{\partial |\psi_I(t)\rangle}{\partial t} = H_{1I}(t) |\psi_I(t)\rangle. \quad (13)$$

It is now easy to obtain a solution for $W(t)$ as a power series in the perturbing Hamiltonian H_1 . First we integrate Eq. (12) between time 0 and time t , obtaining

$$W(t) = 1 + \frac{1}{i\hbar} \int_0^t dt' H_{1I}(t') W(t'), \quad (14)$$

where we have used $W(0) = 1$. This is an exact result, but it is not a solution for $W(t)$, since $W(t)$ appears on the right-hand side. But by substituting the left-hand side of Eq. (14) into the right-hand side, that is, iterating the equation, we obtain

$$W(t) = 1 + \frac{1}{i\hbar} \int_0^t dt' H_{1I}(t') + \frac{1}{(i\hbar)^2} \int_0^t dt' \int_0^{t'} dt'' H_{1I}(t') H_{1I}(t'') W(t''), \quad (15)$$

another exact equation in which the term containing $W(t)$ on the right hand side has been pushed to second order. Substituting Eq. (14) into the right-hand side of Eq. (15) pushes the term in $W(t)$ to third order, etc. Continuing in this way, we obtain a formal power series for $W(t)$,

$$W_I(t) = 1 + \frac{1}{i\hbar} \int_0^t dt' H_{1I}(t') + \frac{1}{(i\hbar)^2} \int_0^t dt' \int_0^{t'} dt'' H_{1I}(t') H_{1I}(t'') + \dots \quad (16)$$

This series is called the *Dyson series*. It is obviously a kind of a series expansion of $W(t)$ in powers of H_1 .

5. The Usual Problem

Let us assume for simplicity that H_0 has a discrete spectrum, and let us write

$$H_0|n\rangle = E_n|n\rangle, \quad (17)$$

where n is a discrete index. The usual problem in time-dependent perturbation theory is to assume that the system is initially in an eigenstate of the unperturbed system, what we will call the “initial” state $|i\rangle$ with energy E_i ,

$$H_0|i\rangle = E_i|i\rangle. \quad (18)$$

This is just a special case of Eq. (17) (with $n = i$). That is, we assume the initial conditions are

$$|\psi_I(0)\rangle = |\psi_S(0)\rangle = |i\rangle. \quad (19)$$

We will be interested in finding the state of the system at a later time,

$$|\psi_I(t)\rangle = W(t)|i\rangle. \quad (20)$$

By applying the Dyson series (16) to this equation, we obtain a perturbation expansion for $|\psi_I(t)\rangle$,

$$|\psi_I(t)\rangle = |i\rangle + \frac{1}{i\hbar} \int_0^t dt' H_{1I}(t')|i\rangle + \frac{1}{(i\hbar)^2} \int_0^t dt' \int_0^{t'} dt'' H_{1I}(t') H_{1I}(t'')|i\rangle + \dots \quad (21)$$

6. Transition Amplitudes

Let us expand the exact solution of the Schrödinger equation in the interaction picture in the unperturbed eigenstates,

$$|\psi_I(t)\rangle = \sum_n c_n(t)|n\rangle, \quad (22)$$

with coefficients $c_n(t)$ that are functions of time. We can solve for these coefficients by multiplying Eq. (22) on the left by the bra $\langle n|$, which gives

$$c_n(t) = \langle n|W_I(t)|i\rangle, \quad (23)$$

showing that $c_n(t)$ is a transition amplitude in the interaction picture, that is, a matrix element of the time-evolution operator $W(t)$ in the interaction picture with respect to the unperturbed eigenbasis. These are not the same as the transition amplitudes (2), which are the matrix elements of $U(t)$ (the time-evolution operator for kets in the Schrödinger picture) with respect to the unperturbed eigenbasis. There is, however, a simple relation between the two. That is, substituting Eq. (10) into Eq. (23), we have

$$c_n(t) = \langle n|U_0(t)^\dagger U(t)|i\rangle = e^{iE_n t/\hbar} \langle n|U(t)|i\rangle, \quad (24)$$

where we have allowed $U_0(t)^\dagger$ to act to the left on bra $\langle n|$. We see that the transition amplitudes in the interaction picture and those in the Schrödinger picture are related by a simple phase factor. The phase factor removes the rapid time evolution of the transition amplitudes in the Schrödinger picture due to the unperturbed system, leaving behind the slower evolution due to H_1 . The transition probabilities are the squares of the amplitudes and are the same in either case,

$$P_n(t) = |c_n(t)|^2 = |\langle n|W(t)|i\rangle|^2 = |\langle n|U(t)|i\rangle|^2. \quad (25)$$

The perturbation expansion of the transition amplitude $c_n(t)$ is easily obtained by multiplying Eq. (21) by the bra $\langle n|$. We write the result in the form,

$$c_n(t) = \delta_{ni} + c_n^{(1)}(t) + c_n^{(2)}(t) + \dots, \quad (26)$$

where the parenthesized numbers indicate the order of perturbation theory, and where

$$c_n^{(1)}(t) = \frac{1}{i\hbar} \int_0^t dt' \langle n|H_{1I}(t')|i\rangle, \quad (27a)$$

$$c_n^{(2)}(t) = \frac{1}{(i\hbar)^2} \int_0^t dt' \int_0^{t'} dt'' \langle n|H_{1I}(t')H_{1I}(t'')|i\rangle, \quad (27b)$$

etc.

We now switch back to the Schrödinger picture in the expressions for the $c_n^{(r)}$. The interaction picture is useful for deriving the perturbation expansion, but the Schrödinger picture is more convenient for subsequent calculations. For $c_n^{(1)}$, we have

$$\begin{aligned} c_n^{(1)}(t) &= \frac{1}{i\hbar} \int_0^t dt' \langle n|U_0^\dagger(t')H_1(t')U_0(t')|i\rangle \\ &= \frac{1}{i\hbar} \int_0^t dt' e^{i\omega_{ni}t'} \langle n|H_1(t')|i\rangle, \end{aligned} \quad (28)$$

where we have allowed $U_0(t')^\dagger$ and $U_0(t')$ to act to the left and right, respectively, on bra $\langle n|$ and ket $|i\rangle$, bringing out the phase factor $e^{i\omega_{ni}t'}$ where ω_{ni} is the Einstein frequency connecting unperturbed states n and i ,

$$\omega_{ni} = \frac{E_n - E_i}{\hbar}. \quad (29)$$

As for $c_n^{(2)}$, it is convenient to introduce a resolution of the identity $\sum |k\rangle\langle k|$ between the two factors of H_{1I} in Eq. (27b) before switching to the Schrödinger picture. This gives

$$c_n^{(2)}(t) = \frac{1}{(i\hbar)^2} \int_0^t dt' \int_0^{t'} dt'' \sum_k e^{i\omega_{nk}t' + i\omega_{ki}t''} \langle n|H_1(t')|k\rangle\langle k|H_1(t'')|i\rangle. \quad (30)$$

From this the pattern at any order of perturbation theory should be clear. In Eq. (30), the states $|k\rangle$ are known as *intermediate states*, the idea being that there is a time sequence as we move from the right to the left in the product of matrix elements, starting with the initial state $|i\rangle$, moving through the intermediate state $|k\rangle$ and ending with the final state $|n\rangle$. Notice that the variables of integration satisfy $0 \leq t'' \leq t' \leq t$.

7. The Case that H_1 is Time-independent

This is about as far as we can go without making further assumptions about H_1 , so that we can do the time integrals. Let us now assume that H_1 is time-independent, an important case in practice. Then the matrix elements are independent of time and can be taken out of the integrals, and the integrals that remain are elementary. For example, in Eq. (28) we have the integral

$$\int_0^t dt' e^{i\omega t'} = 2e^{i\omega t/2} \frac{\sin \omega t/2}{\omega}, \quad (31)$$

so that

$$c_n^{(1)}(t) = \frac{2}{i\hbar} e^{i\omega_{ni}t/2} \left(\frac{\sin \omega_{ni}t/2}{\omega_{ni}} \right) \langle n|H_1|i\rangle. \quad (32)$$

The case of $c_n^{(2)}$ is similar but more complicated. We will return to it later when we have an application of second order time-dependent perturbation theory.

The transition probability $P_n(t)$ can also be expanded in the perturbation series,

$$P_n(t) = |c_n(t)|^2 = |\delta_{ni} + c_n^{(1)}(t) + c_n^{(2)}(t) + \dots|^2. \quad (33)$$

Notice that on taking the square there are cross terms, that is, interference terms between the amplitudes at different orders.

For now we assume that the final state we are interested in is not the the initial state, that is, we take the case $n \neq i$ so the first term in Eq. (33) vanishes, and we work only to first order of perturbation theory. Then we have

$$P_n(t) = |c_n^{(1)}(t)|^2 = \frac{4}{\hbar^2} \left(\frac{\sin^2 \omega_{ni}t/2}{\omega_{ni}^2} \right) |\langle n|H_1|i\rangle|^2. \quad (34)$$

The transition probability depends on time and on the final state n . As for the time dependence, it is contained in the first factor in the parentheses, while both this factor and the matrix element depend on the final state $|n\rangle$. However, the factor in the parentheses depends on the state n only through its energy E_n , which is contained in the Einstein frequency ω_{ni} , while the matrix element depends on all the properties of the state $|n\rangle$, for example, its momentum, spin, etc.

8. The Case of Time-Periodic Perturbations

Another case that is important in practice is when H_1 has a periodic time dependence of the form

$$H_1(t) = Ke^{-i\omega_0 t} + K^\dagger e^{i\omega_0 t}, \quad (35)$$

where ω_0 is the frequency of the perturbation and K is an operator (generally not Hermitian). We call the first and second terms in this expression the positive and negative frequency components of the perturbation, respectively. This case applies, for example, to the interaction of spins or atoms with a given, classical electromagnetic wave.

To find the transition amplitude in this case we substitute Eq. (35) into Eq. (28) and perform the integration, whereupon we obtain two terms,

$$c_n^{(1)}(t) = \frac{2}{i\hbar} \left[e^{i(\omega_{ni}-\omega_0)t/2} \frac{\sin(\omega_{ni}-\omega_0)t/2}{\omega_{ni}-\omega_0} \langle n|K|i\rangle + e^{i(\omega_{ni}+\omega_0)t/2} \frac{\sin(\omega_{ni}+\omega_0)t/2}{\omega_{ni}+\omega_0} \langle n|K^\dagger|i\rangle \right]. \quad (36)$$

For any given final state n , both these terms are present and contribute to the transition amplitude. And when we square the amplitude to get the transition probability, there are cross terms (interference terms) between these two contributions to the amplitude.

Often, however, we are most interested in those final states to which most of the probability goes, which are the states for which one or the other of the two denominators in Eq. (36) is small. For these states we have $\omega_{ni} \mp \omega_0 \approx 0$, or

$$E_n \approx E_i \pm \hbar\omega_0. \quad (37)$$

We see that the first (positive frequency) term is resonant when the system has absorbed a quantum of energy $\hbar\omega_0$ from the perturbation, whereas the second (negative frequency) term is resonant when the system has given up a quantum of energy $\hbar\omega_0$ to the perturbation. We call these two cases *absorption* and *stimulated emission*, respectively.

Taking the case of absorption, and looking only at final states $|n\rangle$ that are near resonance ($E_n \approx E_i + \hbar\omega_0$), we can write the transition probability to first order of perturbation theory as

$$P_n = \frac{4}{\hbar^2} \left[\frac{\sin^2(\omega_{ni}-\omega_0)t/2}{(\omega_{ni}-\omega_0)^2} \right] |\langle n|K|i\rangle|^2. \quad (38)$$

Similarly, for nearly resonant final states in stimulated emission, we have

$$P_n = \frac{4}{\hbar^2} \left[\frac{\sin^2(\omega_{ni} + \omega_0)/2}{(\omega_{ni} + \omega_0)^2} \right] |\langle n | K^\dagger | i \rangle|^2. \quad (39)$$

These formulas may be compared to Eq. (34). In all cases, P_n has a dependence on time that is described by functions of a similar form.

9. How P_n Depends on Time

Let us fix the final state $|n\rangle$ and examine how the probability $P_n(t)$ develops as a function of time in first order time-dependent perturbation theory. To be specific we will take the case of a time-independent perturbation and work with Eq. (34), but with ω_{ni} replaced by $\omega_{ni} \pm \omega_0$ and H_1 replaced by K or K^\dagger , everything we say also applies to absorption or stimulated emission.

Obviously $P_n(0) = 0$ (because $n \neq i$ and all the probability lies in state $|i\rangle$ at $t = 0$). At later times we see that $P_n(t)$ oscillates at frequency ω_{ni} between 0 and a maximum proportional to $1/\omega_{ni}^2$. The frequency ω_{ni} measures how far the final state is “off resonance,” that is, how much it fails to conserve energy. If this frequency is large, the probability $P_n(t)$ oscillates rapidly between zero and a small maximum. But as we move the state $|n\rangle$ closer to the initial state $|i\rangle$ in energy, ω_{ni} gets smaller, the period of oscillations becomes longer, and the amplitude grows.

If there is a final state $|n\rangle$ degenerate in energy with the initial state $|i\rangle$ (not the same state since we are assuming $n \neq i$), then $\omega_{ni} = 0$ and the time-dependent factor in Eq. (34) takes on its limiting value, which is $t^2/4$. In this case, first order perturbation theory predicts that the probability $P_n(t)$ grows without bound, obviously an absurdity after a while since we must have $P_n \leq 1$. This is an indication of the fact that at sufficiently long times first order perturbation theory breaks down and we must take into account higher order terms in the perturbation expansion. In fact, to get sensible results at such long times, it is necessary to take into account an infinite number of terms (that is, to do some kind of summation of the series). But at short times it is correct that P_n for a state on resonance grows as t^2 .

These considerations are important when the system has a discrete spectrum, for example, when a spin is interacting with a time-periodic magnetic field or when we are looking at a few discrete states of an atom in the presence of laser light. These are important problems in practice. Recall that in Notes 14 we solved the Schrödinger equation exactly for a spin in a certain kind of time-periodic magnetic field, but in more general cases an exact solution is impossible and we may have to use time-dependent perturbation theory. It is interesting to compare the exact solution presented in Notes 14 with the perturbative solutions presented here, to see the limitations of the perturbative solutions.

In such problems with a discrete spectrum, the resonance condition may not be satisfied exactly for any final state $n \neq i$. In fact, in problems of emission and absorption, if the frequency ω_0 of the perturbation is chosen randomly, then it is unlikely that the resonant energy $E_i \pm \hbar\omega_0$ will exactly

match any unperturbed eigenstate. In that case, first-order theory predicts that the transition probability to all final states just oscillates in time.

On the other hand, if the final states are members of a continuum, then there is an infinite number of states arbitrarily close to the resonance condition in energy. For those cases, we must examine how the transition probability depends on energy.

10. How P_n Depends on Energy

Now let us fix the time t and examine how the expression for $P_n(t)$ in first order perturbation theory, Eq. (34), depends on the energy E_n of the final state $|n\rangle$ (working for simplicity with the case of a time-independent perturbation). We shall concentrate on the energy dependence of the time-dependent factor in the parentheses, remembering that the matrix element also depends on the energy (and other parameters) of the final state. To do this we plot the function $\sin^2(\omega t/2)/\omega^2$ as a function of ω , as shown in Figs. 1 and 2 for two different times. In the plot, ω is to be identified with $\omega_{ni} = (E_n - E_i)/\hbar$, so that ω specifies the energy of the final state and $\omega = 0$ is the resonance (energy conserving) condition.

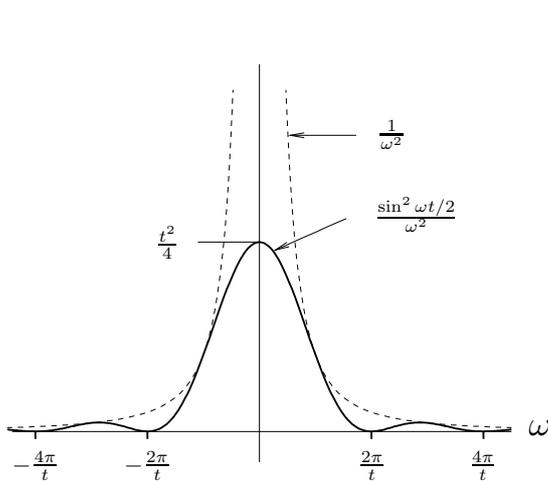


Fig. 1. The function $\sin^2(\omega t/2)/\omega^2$ as a function of ω for fixed t . The dotted curve is the envelope $1/\omega^2$.

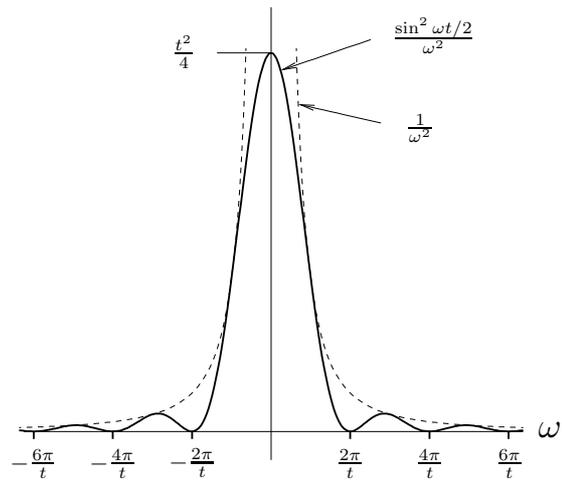


Fig. 2. Same but for a larger value of t . The area of the curve is dominated by the central lobe, and grows in proportion to t .

The curve consists of oscillations under the envelope $1/\omega^2$, with zeroes at $\omega = (2n\pi/t)$. The central lobe has height $t^2/4$ and width that is proportional to $1/t$, so the area of the central lobe is proportional to t . As t increases, the central lobe grows in height and gets narrower, a behavior that reminds us of functions that approach a δ -function, but in this case the limit is not a δ -function because the area is not constant. In fact, the total area is given exactly by an integral that can be

evaluated by contour integration,

$$\int_{-\infty}^{+\infty} d\omega \frac{\sin^2 \omega t/2}{\omega^2} = \frac{\pi t}{2}, \quad (40)$$

showing that the area is indeed proportional to t . Thus if we divide by t we do get a δ -function as $t \rightarrow \infty$,

$$\lim_{t \rightarrow \infty} \frac{1}{t} \frac{\sin^2 \omega t/2}{\omega^2} = \frac{\pi}{2} \delta(\omega). \quad (41)$$

For fixed $\omega \neq 0$ the function under the limit in this expression approaches 0 as $t \rightarrow \infty$, while exactly at $\omega = 0$ it grows in proportion to t , with a constant total area. This is exactly the behavior that produces a δ -function in the limit.

In physical applications we never really go to infinite time, rather we work with times long enough that there is negligible error in replacing the function on the left-hand side of Eq. (41) by its limit. To deal with the case of finite time, we introduce the notation,

$$\frac{\sin^2 \omega t/2}{\omega^2} = \frac{\pi}{2} t \Delta_t(\omega), \quad (42)$$

which defines the function $\Delta_t(\omega)$. Then the limit (41) can be written,

$$\lim_{t \rightarrow \infty} \Delta_t(\omega) = \delta(\omega). \quad (43)$$

As we shall see when we take up some applications, the δ -function in Eq. (41) enforces energy conservation in the limit $t \rightarrow \infty$, that is, only transitions to final states of the same energy as the initial state are allowed in that limit. At finite times, transitions take place to states in a range of energies about the initial energy, given in frequency units by the width of the function $\Delta_t(\omega)$. But as we have seen this width is of order $1/t$, or, in energy units, \hbar/t . This is an example of the energy-time uncertainty relation, $\Delta E \Delta t > \approx \hbar$, indicating that a system that is isolated (not subjected to a measurement) over a time interval Δt has an energy that is uncertain by an amount $\Delta E > \approx \hbar/\Delta t$.

Now we can write the transition probability (34) as

$$P_n(t) = \frac{2\pi t}{\hbar^2} \Delta_t(\omega_{ni}) |\langle n|H_1|i\rangle|^2. \quad (44)$$

This applies in first order perturbation theory, in the case $n \neq i$.

The case $n = i$ is also of interest, and can be analyzed similarly. We will return to this case later in the course.

11. Application: Potential Scattering

To proceed further it is best to look at an application. We will now consider the problem potential scattering of a spinless particle, analyzed by time-dependent perturbation theory. We let the unperturbed Hamiltonian be $H_0 = \mathbf{p}^2/2m$ and we take the perturbation to be $H_1 = U(\mathbf{r})$,

where U is some potential. We do not assume the potential is rotationally invariant, but it should be localized in an appropriate sense. We will examine more carefully the degree of localization required later in the course, when we will also examine other conditions of validity of the theory.

The unperturbed eigenstates are free particle solutions, which we take to be plane waves. In order to deal with discrete final states, we place our system in a large box of side L and volume $V = L^3$, and we adopt periodic boundary conditions. This is equivalent to dividing the universe up into boxes and demanding that all the physics be periodic, that is, the same in all the boxes. We shall assume that the size of the box is much larger than the range of the potential $U(\mathbf{r})$. When we are done we take $V \rightarrow \infty$ to get physical results. We denote the unperturbed eigenstates by $|\mathbf{k}\rangle$, with wave functions

$$\psi_{\mathbf{k}}(\mathbf{r}) = \langle \mathbf{r} | \mathbf{k} \rangle = \frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{\sqrt{V}}, \quad (45)$$

so that

$$\langle \mathbf{k} | \mathbf{k}' \rangle = \delta_{\mathbf{k}, \mathbf{k}'}. \quad (46)$$

Here we are normalizing the eigenfunctions to the volume of the box, and integrating over the volume of the box when forming scalar products as in Eq. (46). The quantized values of \mathbf{k} are given by

$$\mathbf{k} = \frac{2\pi}{L} \mathbf{n}, \quad (47)$$

where $\mathbf{n} = (n_x, n_y, n_z)$ is a vector of integers, each of which ranges from $-\infty$ to $+\infty$. The unperturbed eigenstates can be represented as a lattice of points in \mathbf{k} -space, in which the lattice spacing is $2\pi/L$ and the density is $(L/2\pi)^3 = V/(2\pi)^3$. We let $|\mathbf{k}_i\rangle$ be an incident plane wave (the initial state), and $|\mathbf{k}\rangle$ be some final state.

Notice that the initial state is somewhat unrealistic from a physical standpoint. The initial state is a plane wave $\exp(i\mathbf{k}_i \cdot \mathbf{r})$ that fills up all of space, including the region where $U(\mathbf{r})$ is appreciably nonzero. Let us suppose it is a potential well. Thinking in classical terms, it is as if all of space is filled with particles with exactly the same momentum and energy, even the particles in the middle of the well. Of course a particle coming in from infinity and entering a potential well will gain kinetic energy, and the direction of its momentum will change (this is the scattering process in action). But the particles of our initial state in the middle of the potential have the same kinetic energy and momentum as the particles that are coming in from infinity. Obviously this initial condition would be difficult to establish in practice. Nevertheless, it turns out that these particles with the wrong energy and momentum in the initial state do not affect the transition probabilities after sufficiently long times, and so they do not affect the cross section that we shall compute. All they do is give rise to short-time transients that can be regarded as nonphysical since they arise from the artificialities of the initial conditions. We shall say more about these transients below, but for now we shall just continue to follow the formulas of time-dependent perturbation theory.

In this application the perturbing Hamiltonian is time-independent, so the transition amplitude in first order perturbation theory is given by Eq. (32), with the change of notation $|i\rangle \rightarrow |\mathbf{k}_i\rangle$,

$|n\rangle \rightarrow |\mathbf{k}\rangle$, etc. The transition amplitude is

$$c_{\mathbf{k}}^{(1)}(t) = \frac{2}{i\hbar} e^{i\omega t/2} \left(\frac{\sin \omega t/2}{\omega} \right) \langle \mathbf{k} | U(\mathbf{r}) | \mathbf{k}_i \rangle, \quad (48)$$

where

$$\omega = \frac{E_{\mathbf{k}} - E_{\mathbf{k}_i}}{\hbar} = \frac{\hbar}{2m} (k^2 - k_i^2), \quad (49)$$

and the transition probability is

$$\sum_{\mathbf{k}} \frac{2\pi}{\hbar^2} t \Delta_t(\omega) |\langle \mathbf{k} | U(\mathbf{r}) | \mathbf{k}_i \rangle|^2, \quad (50)$$

where we sum over some set of final states for which $\mathbf{k} \neq \mathbf{k}_i$.

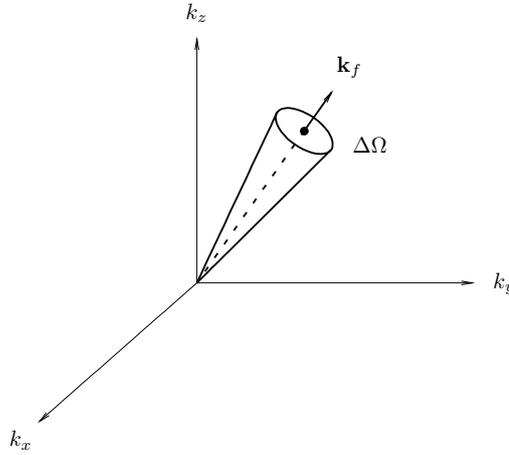


Fig. 3. To compute the differential transition rate $dw/d\Omega$, we sum over all lattice points in \mathbf{k} -space lying in a small cone of solid angle $\Delta\Omega$ centered on some final vector \mathbf{k}_f of interest. The direction $\hat{\mathbf{n}}_f$ of \mathbf{k}_f determines the (θ, ϕ) dependence of the differential cross section.

Which final states \mathbf{k} do we sum over? This depends on what question we wish to ask. If we are interested in the transition rate to any final state, then we sum over all of them (every lattice point in \mathbf{k} -space except \mathbf{k}_i). Often, however, we are interested in more refined information. In the present case, let us sum over all final states (lattice points) that lie in a cone of small solid angle $\Delta\Omega \ll 1$ in \mathbf{k} -space, as illustrated in Fig. 3. Let the cone be centered on a direction $\hat{\mathbf{n}}_f$, a given unit vector pointing toward some counting device in a scattering experiment. Then define a “final wave vector” \mathbf{k}_f by requiring that \mathbf{k}_f have the same direction as $\hat{\mathbf{n}}_f$, and that it satisfy conservation of energy,

$$\frac{\hbar^2 k_f^2}{2m} = \frac{\hbar^2 k_i^2}{2m}, \quad (51)$$

that is, $k_f = k_i$. Then

$$\mathbf{k}_f = k_i \hat{\mathbf{n}}_f. \quad (52)$$

This is only a definition, and although \mathbf{k}_f satisfies energy conservation, notice that the states in the cone that we sum over include states of all energies, from 0 to ∞ .

With this understanding of the states we sum over in the expression (50), we see that we are computing the probability as a function of time that the system will occupy a momentum state lying in the cone. Under some circumstances transition probabilities are proportional to time, and then we can refer to a *transition rate* as the probability per unit time for the process in question. We will generally use the symbol w for transition rates. In the present case, we divide the probability (50) by t and write

$$\frac{dw}{d\Omega} \Delta\Omega = \sum_{\mathbf{k} \in \text{cone}} \frac{2\pi}{\hbar^2} \Delta_t(\omega) |\langle \mathbf{k} | U(\mathbf{r}) | \mathbf{k}_i \rangle|^2, \quad (53)$$

where $dw/d\Omega$ is the transition rate per unit solid angle, a quantity that is generally a function of direction, in this case, the direction $\hat{\mathbf{n}}_f$.

Notice that the factors of t have cancelled in Eq. (53), but the right-hand side still depends on t through $\Delta_t(\omega)$. If, however, t is large enough that $\Delta_t(\omega)$ can be replaced by $\delta(\omega)$, then the right hand side does become independent of t , and the transition rate is meaningful. We see that at short times we do not have a transition rate, but that at longer times we do.

For now let us assume that t is large enough that $\Delta_t(\omega)$ can be replaced by $\delta(\omega)$, since this gives the simplest answer. Later we will examine quantitatively how long we must wait for this to be true. Using Eq. (49), we can transform $\delta(\omega)$ by the rules for δ -functions,

$$\delta(\omega) = \frac{m}{\hbar k_i} \delta(k - k_i). \quad (54)$$

We must also take the limit $V \rightarrow \infty$ to obtain physical results. In this limit, the initial wave function $\psi_{\mathbf{k}}(\mathbf{r})$ loses meaning (it goes to zero everywhere, since it is normalized to unity over the volume of the box), as does the differential transition rate $dw/d\Omega$. However, the differential cross section $d\sigma/d\Omega$, which is the differential transition rate normalized by the incident flux, is well defined in the limit. The incident flux is

$$J_{\text{inc}} = n_i v_i = \frac{1}{V} \frac{\hbar k_i}{m}, \quad (55)$$

where $n_i = 1/V$ is the number of particles per unit volume in the incident state, and $v_i = \hbar k_i/m$ is the incident velocity. Thus

$$\frac{d\sigma}{d\Omega} = \frac{Vm}{\hbar k_i} \frac{dw}{d\Omega}. \quad (56)$$

Also, in the limit $V \rightarrow \infty$, the sum over lattice points \mathbf{k} in Eq. (53) can be replaced by an integral,

$$\sum_{\mathbf{k} \in \text{cone}} \rightarrow \frac{V}{(2\pi)^3} \int_{\text{cone}} d^3\mathbf{k} = \frac{V}{(2\pi)^3} \Delta\Omega \int_0^\infty k^2 dk, \quad (57)$$

where $V/(2\pi)^3$ is the density of states per unit volume in \mathbf{k} -space and where we have switched to spherical coordinates in \mathbf{k} -space and done the angular integral over the narrow cone.

Finally we evaluate the matrix element in Eq. (53). It is

$$\langle \mathbf{k} | U(\mathbf{r}) | \mathbf{k}_i \rangle = \int d^3 \mathbf{r} \psi_{\mathbf{k}}^*(\mathbf{r}) U(\mathbf{r}) \psi_{\mathbf{k}_i}(\mathbf{r}) = \frac{1}{V} \int d^3 \mathbf{r} e^{-i(\mathbf{k}-\mathbf{k}_i) \cdot \mathbf{r}} U(\mathbf{r}) = \frac{(2\pi)^{3/2}}{V} \tilde{U}(\mathbf{k} - \mathbf{k}_i), \quad (58)$$

where we use Eq. (45) and define the Fourier transform $\tilde{U}(\mathbf{q})$ of the potential $U(\mathbf{r})$ by

$$\tilde{U}(\mathbf{q}) = \int \frac{d^3 \mathbf{r}}{(2\pi)^{3/2}} e^{-i\mathbf{q} \cdot \mathbf{r}} U(\mathbf{r}). \quad (59)$$

Putting all the pieces together, we have

$$\begin{aligned} \frac{d\sigma}{d\Omega} &= \frac{Vm}{\hbar k_i} \frac{1}{\Delta\Omega} \frac{V}{(2\pi)^3} \Delta\Omega \int_0^\infty k^2 dk \frac{2\pi}{\hbar^2} \frac{m}{\hbar k_i} \delta(k - k_i) \frac{(2\pi)^3}{V^2} |\tilde{U}(\mathbf{k} - \mathbf{k}_i)|^2 \\ &= \frac{2\pi}{\hbar^2} \left(\frac{m}{\hbar k_i} \right)^2 \int_0^\infty k^2 dk \delta(k - k_i) |\tilde{U}(\mathbf{k} - \mathbf{k}_i)|^2, \end{aligned} \quad (60)$$

where the factors of V and $\Delta\Omega$ have cancelled, as they must. Notice that \mathbf{k} under the integral is a vector, but only its magnitude k is a variable of integration. The direction of \mathbf{k} is that of the small cone, that is, $\mathbf{k} = k\hat{\mathbf{n}}_f$. Now the δ -function makes the integral easy to do. In particular, $\mathbf{k} = k\hat{\mathbf{n}}_f$ becomes $k_i\hat{\mathbf{n}}_f = k_f\hat{\mathbf{n}}_f = \mathbf{k}_f$. Notice that if t is large enough to make the replacement $\Delta_t(\omega) \rightarrow \delta(\omega)$ but not infinite, the function $\delta(k - k_i)$ should be understood as a function of small but nonzero width. Thus after finite time t the transitions are actually taking place to states that lie in a small energy range about the initial energy. This is an important point: in time-dependent perturbation theory, we do not attempt to enforce energy conservation artificially, rather our job is to solve the Schrödinger equation, and when we do we find that energy conservation emerges in the limit $t \rightarrow \infty$.

The final answer is now easy. It is

$$\frac{d\sigma}{d\Omega} = 2\pi \frac{m^2}{\hbar^4} |\tilde{U}(\mathbf{k}_f - \mathbf{k}_i)|^2. \quad (61)$$

Notice that the momentum transfer in the scattering process is

$$\mathbf{p}_f - \mathbf{p}_i = \hbar(\mathbf{k}_f - \mathbf{k}_i), \quad (62)$$

and the differential cross section is a function of this momentum transfer. This result from first-order time-dependent perturbation theory is the same as that obtained in the first Born approximation, to be considered later in the course. As we shall see, the result (61) is valid in the high-energy limit, in which the exact wave function in the midst of the potential does not differ much from the unperturbed wave function.

12. Short-Time Behavior

Let us now estimate the time after which the replacement $\Delta_t(\omega) \rightarrow \delta(\omega)$ becomes valid. Let us call this time t_1 , which we shall estimate as an order of magnitude.

The function $\Delta_t(\omega)$ has a width in ω given by $\Delta\omega = 1/t$, as an order of magnitude, or, in energy units, $\Delta E = \hbar/t$. We can convert this to wavenumber units by using

$$\Delta E = \frac{\hbar^2 k \Delta k}{m}, \quad (63)$$

or,

$$\Delta k = \frac{m}{\hbar k t}. \quad (64)$$

This is the width of the function we are writing as $\delta(k - k_i)$ under the integral in Eq. (60). The replacement of this function by an exact delta function is valid if this Δk is much less than the scale of variation of the function $\tilde{U}(k\hat{\mathbf{n}}_f - \mathbf{k}_i)$ with respect to k , that is, the increment in k over which \tilde{U} undergoes a significant change. To estimate this, let us suppose that the potential $U(\mathbf{r})$ has a range (in real space) of a , that is, it falls to zero rapidly outside this radius. Then the Fourier transform \tilde{U} will have a width of order $1/a$ with respect to k . Thus, the condition under which $\Delta_t(\omega)$ can be replaced by $\delta(\omega)$ is

$$\frac{m}{\hbar k t} \ll \frac{1}{a}, \quad (65)$$

or,

$$t \gg t_1 = \frac{am}{\hbar k} = \frac{a}{v}, \quad (66)$$

where v is the velocity of the particles in the incident beam. But this is of the order of the time it takes for one of these particles to traverse the range of the potential, that is, it is approximately the time over which the scattering takes place.

It is also the time required for the “unphysical” particles in the initial state, the ones that find themselves in the midst of the potential at $t = 0$ with the wrong energy and momentum, to get scattered out of the potential and to be replaced by new particles that come in from the incident beam. As these particles are scattered also, there develops a “front” of scattered particles, moving away from the scatterer, while a steady state develops behind the front. As time goes on, the unphysical particles become proportionally unimportant in the accounting of the transition rate. Thus the transients at times $t < t_1$ in the solution of the Schrödinger equation are related to the artificiality of the initial conditions.

This line of physical reasoning is essentially classical, but it suggests that at a fixed distance from the scatterer, the exact time-dependent solution of the Schrödinger equation, the wave function $\psi_S(\mathbf{r}, t) = \langle \mathbf{r} | U(t) | \mathbf{k}_i \rangle$ in the Schrödinger picture, actually approaches a quantum stationary state, that is, an energy eigenfunction of the full Hamiltonian $H_0 + H_1$, in the limit $t \rightarrow \infty$. This eigenfunction has the time dependence $e^{-iE_i t/\hbar}$, that is, it has the same energy as the free particle state $|\mathbf{k}_i\rangle$. One must simply wait for the front and any dispersive tail trailing behind it to pass, and then one has a steady stream of outgoing particles. To be careful about this argument, one must worry about bound states of the potential, which correspond to the unphysical particles in the classical picture whose energy is too low to escape from the potential well. We will not pursue this line of

reasoning further, but it is an example of how the time-dependent and time-independent points of view are related to one another and how they permeate scattering theory.

Later we will see other examples of short-time transients in other applications of time-dependent perturbation theory, and they always represent nonphysical effects having to do with the artificiality of the initial conditions. We can ignore them if all we want are physical answers.

13. Example: The Yukawa Potential

To make an application of Eq. (61), let us choose the Yukawa potential,

$$U(r) = A \frac{e^{-\kappa r}}{r}, \quad (67)$$

where A and κ are constants. Yukawa invented his potential originally to represent the forces between nucleons. He assumed the nuclear forces were mediated by a boson, the particle that we now know as the π -meson, which has mass $M \approx 140 \text{ MeV}/c^2$. This particle has the Compton wave length

$$\lambda_C = \frac{\hbar}{Mc} \approx 1.4 \times 10^{-13} \text{ cm}, \quad (68)$$

which is approximately the range of the nuclear forces. The parameter κ in the Yukawa potential is the inverse Compton wavelength,

$$\kappa = \frac{Mc}{\hbar}. \quad (69)$$

The Yukawa potential arises as the static solution of the Klein-Gordon equation with a point source, the relativistic wave equation for a spin-0 particle. That is, it is the Green's function for the time-independent Klein-Gordon equation.

In the limit $M \rightarrow 0$, the Klein-Gordon equation goes over to the ordinary wave equation, corresponding to the massless photon. Likewise, the Yukawa potential in this limit becomes the Coulomb potential, which is the Green's function for the Laplace equation, the static limit of the wave equation. The Coulomb potential describes the electromagnetic field produced by a static, point charge, and the Yukawa potential plays a similar role for fields in which the force is mediated by a massive particle. Today we have a much more sophisticated understanding of nuclear forces than in Yukawa's day, but the Yukawa potential is still useful for modeling purposes.

To apply Eq. (61) we need only compute the Fourier transform, as defined by Eq. (59), of the Yukawa potential. Since the Yukawa potential is rotationally invariant, its Fourier transform is too, so $\tilde{U}(\mathbf{q})$ depends only on the magnitude $q = |\mathbf{q}|$. Setting $\mathbf{q} = q\hat{\mathbf{z}}$, the Fourier transform is easy to evaluate in spherical coordinates, yielding,

$$\tilde{U}(\mathbf{q}) = \frac{2A}{(2\pi)^{1/2}} \frac{1}{\kappa^2 + q^2}. \quad (70)$$

Now setting $\mathbf{q} = \mathbf{k} - \mathbf{k}_i$ (where we now write simply \mathbf{k} instead of \mathbf{k}_f for the final wave vector), we have

$$q^2 = 4k^2 \sin^2 \theta/2, \quad (71)$$

where θ is the angle between \mathbf{k} and \mathbf{k}_i , that is, it is the scattering angle. Then the cross section is

$$\frac{d\sigma}{d\Omega} = \frac{4A^2m^2}{\hbar^4} \frac{1}{(4k^2 \sin^2 \theta/2 + \kappa^2)^2}. \quad (72)$$

This result depends on several parameters (A , m , κ and k), and it is valid only for certain ranges of them. We will examine the validity of this result later, but basically it is valid when the energy of the incident particles is high.

An obvious thing to do with the cross section (72) is to take the limit $M \rightarrow 0$, that is, $\kappa \rightarrow 0$, hopefully to obtain the cross section for Coulomb scattering. We may also set $A = Z_1 Z_2 e^2$, so that the potential becomes

$$U(r) = \frac{Z_1 Z_2 e^2}{r}, \quad (73)$$

the Coulomb potential for the scattering of two particles of charges $Z_1 e$ and $Z_2 e$. Then we find

$$\frac{d\sigma}{d\Omega} = \frac{Z_1^2 Z_2^2 e^4 m^2}{4\hbar^4 k^4} \frac{1}{\sin^4 \theta/2} = \frac{Z_1^2 Z_2^2 e^4}{16E^2 \sin^4 \theta/2}, \quad (74)$$

which we recognize as the Rutherford cross section.

The Rutherford cross section is the exact cross section for nonrelativistic, classical scattering of charged particles. It also happens to be the exact cross section for nonrelativistic scattering of distinguishable charged particles in the electrostatic approximation in quantum mechanics, although we have not proved that with our derivation because we have only computed the first term of a perturbation series. To prove that fact, it is necessary to solve the quantum problem of Coulomb scattering exactly, something that can be done by separating the wave equation in confocal parabolic coordinates.

But before we get too excited about having derived the exact answer by the use of perturbation theory, it should be pointed out that the conditions of validity on the formula (61) are not met for any ranges of the parameters. In other words, it is a fluke that the answer came out right. If we compare our results to the exact solution, we find out that although our cross section is exactly correct, the scattering amplitude is completely wrong. But it is wrong only because it has the wrong phase, something that cancels out when we take the square.

The phase of the scattering amplitude becomes important if we consider identical particles, for which the wave function must be composed of properly symmetrized or antisymmetrized wave functions. In this case the scattering amplitude is the sum of two terms, and if we get the phases of the amplitudes wrong, then the cross terms in the expression for the cross section are all wrong.

14. Other Applications

Here are some other applications of time-dependent perturbation theory that we will consider later in the course. As an example of an atom interacting with a classical light wave, we shall study the photoelectric effect in the next set of notes. In the photoelectric effect, a high energy

photon, described by a classical light wave, ejects an electron from an atom, leaving behind a positive ion. Later we will consider the emission and absorption of radiation by an atom using the quantized theory of the electromagnetic field, that is, we will study the emission and absorption of photons. A similar example, one that requires second-order time-dependent perturbation theory, is the scattering of photons by matter. Later still we will consider a variety of relativistic processes that are applications of time-dependent perturbation theory, including relativistic scattering of charged particles and the creation and annihilation of electron-positron pairs.

Problems

1. Some questions involving the scattering of identical particles.

(a) In classical mechanics we can always distinguish particles by placing little spots of paint on them. Suppose we have two particles in classical mechanics that are identical apart from insignificant spots of blue and green paint. (The spots have no effect on the scattering.) Suppose the differential cross section in the center-of-mass system for the detection of blue particles is $(d\sigma/d\Omega)(\theta, \phi)$. What is the differential cross section $(d\sigma/d\Omega)_{dc}(\theta, \phi)$ for the detection of particles when we don't care about the color?

(b) Consider the scattering of two identical particles of spin j in quantum mechanics. Work in the center-of-mass system, and let $\mu = m/2$ be the reduced mass. Consider in particular three cases: $j = 0$, $j = \frac{1}{2}$, and $j = 1$. Organize the eigenstates of $H_0 = p^2/2\mu$ as tensor products of spatial states times spin states; make the spin states eigenstates of S^2 and S_z , where $\mathbf{S} = \mathbf{J}_1 + \mathbf{J}_2$, and make the spatial states properly symmetrized or antisymmetrized plane waves. Let the initial spin state be $|S_i M_{S_i}\rangle$ and the final one be $|S_f M_{S_f}\rangle$. Since potential scattering cannot flip the spin, the cross section will be proportional to $\delta(S_i, S_f)\delta(M_{S_i}, M_{S_f})$. Find the differential cross section in terms of

$$\tilde{U}_+ = \tilde{U}(\mathbf{k}_f + \mathbf{k}_i), \quad \tilde{U}_- = \tilde{U}(\mathbf{k}_f - \mathbf{k}_i), \quad (75)$$

where \tilde{U} is defined as in Eq. (59). Use the fact that $U(\mathbf{r}) = U(-\mathbf{r})$ to simplify the result as much as possible. Use notation like that in Eq. (61).

(c) For the three cases $j = 0$, $j = \frac{1}{2}$, $j = 1$, assume that the initial state is unpolarized and that we do not care about the final spin state. Find the differential cross section in terms of the quantities $a = |\tilde{U}_+|^2$, $b = |\tilde{U}_-|^2$, and $c = \text{Re}(\tilde{U}_+^* \tilde{U}_-)$.

(d) Work out the answer for the case of Coulomb scattering of two electrons, and compare to the classical Rutherford formula, Eq. (74). Express your answer in a notation similar to that of Eq. (74). The cross term you get in applying the results of part (c) to Coulomb scattering is actually incorrect; the trouble is that plane waves do not adequately represent the unbound Coulomb wave functions, which have long range, logarithmic phase shifts. The correct answer is called the Mott cross section, which we will discuss later in class.