Physics 221B
Spring 2012
Notes 42
Scattering of Radiation by Matter

1. Introduction

In the previous set of Notes we treated the emission and absorption of radiation by matter. In these Notes we turn to the scattering of radiation by matter. As before, the material system in question can be almost anything (atom, molecule, nucleus, etc), but when it is necessary to be specific we shall for simplicity assume that it is a single-electron atom. The formalism is easily extended to other types of material systems.

We shall see that in a certain sense the emission and absorption of radiation are special cases of the scattering of radiation, in which the frequency of the initial photon is close to a resonance frequency of the material system (the Einstein frequency connecting two energy eigenstates). In such cases it is partly a matter of preference how one should view the process, but in some respects the scattering point of view is more fundamental and elegant.

2. Applications

The applications of the theory developed in these Notes are very broad. Almost any situation in which radiation passes through a gas affords an example of the physics we shall describe here. For example, in infrared and Raman scattering experiments radiation is passed through an molecular gas and the absorption spectrum or scattering cross section is measured, providing a primary source of information about the structure of molecules.

Another example involves radiation passing through the Earth's atmosphere. The atmosphere is mostly transparent to sunlight, but there is some scattering, especially at the higher (blue) frequencies. This is Rayleigh scattering, which we shall consider later. The higher frequencies are more strongly scattered because they are closer to certain resonances in the ultraviolet. As we shall see, the cross section for Rayleigh scattering rises rapidly as a function of frequency as we approach a resonance. This is the reason the sky is blue: When we look at a part of the sky away from the sun, the blue light we see is sunlight scattered by the air along our line of sight.

The Earth in turn radiates thermal radiation in the infrared that must pass through the atmosphere to reach outer space where it escapes. This radiation has a frequency range that covers the vibrational transitions of most simple molecules, so it is strongly scattered by several types of molecules such as the greenhouse gases CO_2, H_2O and CH_4. Thus an infrared photon leaving the Earth's surface must diffuse through the atmosphere in a random walk, a process that is much slower than passing straight through. The greenhouse gases act like a blanket, keeping the Earth warm.

The oxygen and nitrogen that are the major components of the atmosphere do not scatter infrared radiation, because they are homonuclear diatomic molecules which because of symmetry do not have a permanent electric dipole moment. Notice that the atmosphere makes it easy for radiation to get in at optical frequencies, and difficult to get back out at infrared frequencies.

There are many examples in astrophysics where the scattering or absorption of radiation by matter is important. For example, sunlight passing through the cooler outer layers of the sun's atmosphere produces an absorption spectrum (the dark Fraunhoffer lines) that give information about the chemical species occurring in the sun and the physical conditions in its atmosphere. Similar information is available for other stars. For another example, transport of energy by radiation is important in the interior of stars, in which photons undergo repeated (Thomson) scattering by free electrons in the plasma and slowly diffuse upward toward the surface. In many stars such as the sun this radiative transport dominates the energy transport at certain radii (at other radii convective transport is dominant).

The interaction of photons with matter is also important in nuclear physics. In the Mössbauer effect, for example, gamma ray photons emitted in the decay of a nucleus are used to excite other nuclei, lifting them from their ground state into an excited state. The resonance is very narrow, however, and the photon can be shifted out of resonance by a Doppler shift involving only small velocities. The Mössbauer effect provided the first clear experimental demonstration of the red shift that photons suffer on climbing out of a gravitational field. This effect implies that clocks run at different rates in different regions of a gravitational field. It is one of the conceptual corner stones of general relativity.

3. The Scattering Problem

We shall consider the reaction

$$A + \gamma \to B + \gamma', \tag{1}$$

in which an atom in state A interacts with an incident photon γ, which leaves the atom in state B and produces the scattered photon γ'. We will write $\lambda = (\mathbf{k}\mu)$, $\lambda' = (\mathbf{k}'\mu')$ for the modes of the incident and scattered photons, where μ is a polarization index, as described in Sec. 38.12. We will assume that $\lambda \neq \lambda'$, since otherwise there is no scattering. If $A = B$, the scattering is elastic (the initial and final atomic states are the same), and by conservation of energy we have $\omega = \omega'$, where ω and ω' are the frequencies of the photons with modes λ and λ'. If $A \neq B$, the scattering is inelastic, and we have $\omega \neq \omega'$. In this case the final atomic state B may either be higher or lower in energy than the initial state A, depending on circumstances.

There is one photon in both the initial and final states. We will write the initial state $|i\rangle$ and the final state $|n\rangle$ in a variety of ways,

$$\begin{aligned} |i\rangle &= |A\rangle a_\lambda^\dagger |0\rangle = |A\rangle|\lambda\rangle = |A\lambda\rangle, \\ |n\rangle &= |B\rangle a_{\lambda'}^\dagger |0\rangle = |B\rangle|\lambda'\rangle = |B\lambda'\rangle. \end{aligned} \tag{2}$$

We use the index n to label a variable final state, as we did in our presentation of time-dependent perturbation theory in Notes 32; as usual, we will have to sum over collections of final states to get physically relevant probabilities. The energies of the initial and final states are

$$\begin{aligned} E_i &= E_A + \hbar\omega, \\ E_n &= E_B + \hbar\omega', \end{aligned} \tag{3}$$

where E_A and E_B are the energies of the two atomic states, so the Einstein frequency connecting the initial and final states is

$$\omega_{ni} = \frac{E_n - E_i}{\hbar} = \omega_{BA} + \omega' - \omega, \tag{4}$$

where $\omega_{BA} = (E_B - E_A)/\hbar$.

The problem will be to compute the differential cross section $d\sigma/d\Omega'$, where Ω' refers to the direction of the outgoing photon (in mode λ'). The differential cross section is a function of the modes of the initial and final photons λ and λ' and the two atomic states A and B.

4. The Transition Amplitude Vanishes at First Order

We will take the Hamiltonian for the interaction of the matter with the radiation to be $H = H_0 + H_1 + H_2$, where

$$H_0 = \frac{\mathbf{p}^2}{2m} + U(\mathbf{x}) + \sum_\lambda \hbar\omega_\lambda\, a_\lambda^\dagger a_\lambda, \tag{5a}$$

$$H_1 = \frac{e}{mc}[\mathbf{p}\cdot\mathbf{A}(\mathbf{x}) + \mathbf{S}\cdot\mathbf{B}(\mathbf{x})], \tag{5b}$$

$$H_2 = \frac{e^2}{2mc^2}\mathbf{A}(\mathbf{x})^2. \tag{5c}$$

The potential $U(\mathbf{x})$ allows us to describe any single-electron atom (not only hydrogen).

The transition amplitude in first order time-dependent perturbation theory is given by Eq. (32.32), which we reproduce here:

$$c_n^{(1)}(t) = \frac{2}{i\hbar} e^{i\omega_{ni}t/2}\Big(\frac{\sin\omega_{ni}t/2}{\omega_{ni}}\Big)\langle n|H_1|i\rangle. \tag{6}$$

This equation is written in the general notation of Notes 32. For the present application, we identify states $|i\rangle$ and $|n\rangle$ with the states in Eq. (2), so that ω_{ni} is given by Eq. (4), and we identify H_1 with the term H_1 in Eq. (5b). We ignore H_2 in Eq. (5c) since for the moment we are only working to first order. Then the matrix element in Eq. (6) becomes

$$\langle n|H_1|i\rangle = \frac{e}{mc}\langle B\lambda'|[\mathbf{p}\cdot\mathbf{A}(\mathbf{x}) + \mathbf{S}\cdot\mathbf{B}(\mathbf{x})]|A\lambda\rangle. \tag{7}$$

The fields $\mathbf{A}$ and $\mathbf{B}$ have Fourier series (40.20) and (40.22) in terms of the modes of the field. If we write out these series, suppressing all factors except the creation and annihilation operators, then they have the structure,

$$\mathbf{A}, \mathbf{B} = \sum_{\lambda_1}\big(a_{\lambda_1}\ldots a_{\lambda_1}^\dagger\big), \tag{8}$$

where we are careful to use the index λ_1 as a dummy variable of summation, so as not to confuse it with the indices λ and λ' of the incident and scattered photons.

Now focusing on the field part of the matrix element (7), we see that the annihilation operator a_{λ_1} does not contribute to the transition amplitude, because it acts on a state with a single photon, $|A\lambda\rangle$, and either produces a state with zero photons (if $\lambda_1 = \lambda$) or annihilates it (if $\lambda_1 \neq \lambda$). In either case, the resulting state is orthogonal to the state $|B\lambda'\rangle$, and gives zero when the scalar product is taken. Similarly, the creation operator $a^\dagger_{\lambda_1}$ in the Fourier series (8) acts on the single photon state $|A\lambda\rangle$ and produces a two-photon state, which is necessarily orthogonal to any one-photon state such as $|B\lambda'\rangle$. Again, the field part of the scalar product vanishes. Thus we find

$$\langle n|H_1|i\rangle = 0, \tag{9}$$

and there is no contribution to the scattering amplitude at first order of time-dependent perturbation theory. We must go to second-order to find a nonvanishing contribution.

5. Second-Order Time-Dependent Perturbation Theory

This is the first time we have had an application of second-order time-dependent perturbation theory, so we shall return to the formalism of Notes 32 and develop the theory at second order, using the notation of those Notes. In particular, the Hamiltonian is $H = H_0 + H_1$, without any term H_2 as we have in Eq. (5c) above. The second-order contribution to the transition amplitude $c_n(t)$ in the interaction picture is given by Eq. (32.30) in the general case in which H_1 in the Schrödinger picture is allowed to depend on time. For our scattering application, H_1 is time-independent, so we can do the time integrations appearing in Eqs. (32.27). The integral in the first order term in Eq. (32.27a) was done already in Sec. 32.7, with the result shown in Eq. (32.32) and reproduced above in Eq. (6). As for the integrals in the second order term in Eq. (32.27b), we first do the t'' integration, finding,

$$c_n^{(2)}(t) = \frac{1}{(i\hbar)^2}\int_0^t dt' \sum_k e^{i\omega_{nk}t'}\Big(\frac{e^{i\omega_{ki}t'}-1}{i\omega_{ki}}\Big)\langle n|H_1|k\rangle\langle k|H_1|i\rangle. \tag{10}$$

Recall that the sum on k is a sum over "intermediate states" that came from the insertion of a resolution of the identity between the two Hamiltonian factors in Eq. (32.27b). We combine the phase factors in Eq. (10), using the identity,

$$\omega_{nk} + \omega_{ki} = \omega_{ni}, \tag{11}$$

and then we do the t' integration,

$$\begin{aligned} c_n^{(2)}(t) &= \frac{1}{(i\hbar)^2}\int_0^t dt' \sum_k \frac{1}{i\omega_{ki}}(e^{i\omega_{ni}t'} - e^{i\omega_{nk}t'})\langle n|H_1|k\rangle\langle k|H_1|i\rangle \\ &= \frac{1}{(i\hbar)^2}\sum_k \frac{1}{i\omega_{ki}}\Big[\Big(\frac{e^{i\omega_{ni}t}-1}{i\omega_{ni}}\Big) - \Big(\frac{e^{i\omega_{nk}t}-1}{i\omega_{nk}}\Big)\Big]\langle n|H_1|k\rangle\langle k|H_1|i\rangle. \end{aligned} \tag{12}$$

Of the two major time-dependent factors in the square brackets in Eq. (12), the first one,

$$\frac{e^{i\omega_{ni}t}-1}{i\omega_{ni}} = 2e^{i\omega_{ni}t/2}\,\frac{\sin\omega_{ni}t/2}{\omega_{ni}}, \tag{13}$$

is the same time-dependent factor that appears in the first order term $c_n^{(1)}(t)$ shown in Eq. (6). Notice that this factor is independent of k and can be taken out of the sum in Eq. (12). When squared to produce a probability, this factor produces a quantity proportional to time multiplied times a function of frequency that gets narrower as time gets longer,

$$\frac{\sin^2\omega t/2}{\omega^2} = \frac{\pi}{2}\,t\,\Delta_t(\omega), \tag{14}$$

where

$$\lim_{t\to\infty}\Delta_t(\omega) = \delta(\omega). \tag{15}$$

See Eqs. (32.42) and (32.43). The fact that the result is proportional to time is essential for getting a transition rate (a probability per unit time), and the emerging δ-function in the limit $t\to\infty$ is necessary for energy conservation, as explained in Notes 32. In fact, as explained in Sec. 32.13, we do not really have to take t to ∞, it need only be long enough for certain initial transients to die away. These transients are related to the artificiality of the initial conditions, and are nonphysical.

The initial conditions for the scattering problem considered in these Notes contain an artificial element, as did the initial conditions in the potential scattering problem considered in Sec. 32.12. That is, we are assuming that at $t=0$ the atom is known to be in the state A and the field consists of a single photon in mode λ. This mode is a plane wave that fills up all of space, including the region occupied by the atom. It would be impossible to set up such initial conditions experimentally, since there is no way for a light wave to get into the region occupied by the atom without interacting with it. A more realistic set of initial conditions would be a wave packet made up out of single photon states that initially is remote from the atom and not interacting with it. To treat such wave packets, however, would require a more sophisticated formalism than we are using here, so we will stick with the initial conditions we have chosen. The price we pay, however, is the appearance of initial transients without physical significance.

The second major time-dependent term inside the square brackets in Eq. (12) is just such a transient. This term, when squared, does not produce something proportional to time, but rather just gives bounded oscillations that go to zero in the limit $t\to\infty$ after we divide by time. Thus, they do not contribute to the transition rate. This is because the frequency ω_{nk} occurring in that term is not independent of k. The same is true for the cross terms that arise when the sum of the two major time-dependent terms in Eq. (12) is squared. Thus, if all we are interested in is the transition rate and not the initial transients, we can drop the second major time-dependent term in Eq. (12).

The result is an effective transition amplitude at second order that is proportional to the time-dependent factor (13), the same factor that occurs at first order. Combining the first and second

order terms, we obtain an effective transition amplitude,

$$c_n^{\rm eff}(t) = \frac{2}{i\hbar} e^{i\omega_{ni}t/2}\Big(\frac{\sin\omega_{ni}t/2}{\omega_{ni}}\Big)\Big[\langle n|H_1|i\rangle + \sum_k \frac{\langle n|H_1|k\rangle\langle k|H_1|i\rangle}{E_i - E_k}\Big], \tag{16}$$

where we have taken the denominator ω_{ki} appearing in Eq. (12) and written it as $-(E_i - E_k)/\hbar$. The result is the "energy denominator" seen in the second order contribution in Eq. (16). Recall that we had such energy denominators also in second-order bound state perturbation theory (see Notes 21). We drop the zeroth order contribution δ_{ni} to the transition amplitude since for our scattering problem $n \neq i$ (since $\lambda \neq \lambda'$).

6. The Photon Scattering Amplitude at Second Order

For our application the notation H_1 of Notes 32 and Sec. 5 must be replaced by $H_1 + H_2$, given by Eqs. (5). In particular, we must make this replacement in the transition amplitude (16). For example, the first order matrix element in Eq. (16) is replaced by

$$\langle n|H_1 + H_2|i\rangle. \tag{17}$$

The Hamiltonian in Eq. (5) is ordered in powers of the fine structure constant $\alpha \approx 1/137$, as is most easily seen in atomic units where $e = m = \hbar = 1$ and $1/c = \alpha$. Thus, the H_1 term in the matrix element (17) is of order α. This term, however, vanishes, as we found in Sec. 4. To compute the transition amplitude to order α^2, we must keep the H_2 term in the matrix element (17), and interpret the H_1 in the second order term of Eq. (16) as the H_1 in Eq. (5b), dropping H_2 since this will contribute only at third or fourth order of α. Thus, the effective transition amplitude for our scattering problem, valid through order α^2, is

$$c_n^{\rm eff}(t) = \frac{2}{i\hbar} e^{i\omega_{ni}t/2}\Big(\frac{\sin\omega_{ni}t/2}{\omega_{ni}}\Big)\Big[\langle n|H_2|i\rangle + \sum_k \frac{\langle n|H_1|k\rangle\langle k|H_1|i\rangle}{E_i - E_k}\Big], \tag{18}$$

where now H_1 and H_2 are given by Eqs. (5) and states $|i\rangle$ and $|n\rangle$ are given by Eqs. (2). One term involves H_2 taken in first order perturbation theory, and the other involves H_1 taken twice at second order perturbation theory.

7. H_2 in First-Order Perturbation Theory

We begin with the term

$$\langle n|H_2|i\rangle = \frac{e^2}{2mc^2}\langle B\lambda'|\mathbf{A}(\mathbf{x})^2|A\lambda\rangle. \tag{19}$$

Squaring the Fourier series (40.20) for $\mathbf{A}$, we obtain a product series with the structure,

$$\mathbf{A}(\mathbf{x})^2 \sim \sum_{\lambda_1\lambda_2} (a_{\lambda_1}\ldots a^\dagger_{\lambda_1})\cdot(a_{\lambda_2}\ldots a^\dagger_{\lambda_2}), \tag{20}$$

where we suppress all factors except the creation and annihilation operators. This allows us to concentrate on the photon part of the matrix element (19). We see that there are four types of products of creation and annihilation operators that occur in $\mathbf{A}^2$. The product of the two annihilation operators $a_{\lambda_1}a_{\lambda_2}$ does not contribute to the transition amplitude, since it acts on the single photon state $|A\lambda\rangle$ producing zero. Likewise, the product of the two creation operators $a^\dagger_{\lambda_1}a^\dagger_{\lambda_2}$ does not contribute, since it acts on $|A\lambda\rangle$ creating a three-photon state that is orthogonal to the one-photon state $|B\lambda'\rangle$. The product of the annihilation operator times the creation operator, $a_{\lambda_1}a^\dagger_{\lambda_2}$, does contribute, however, as long as $\lambda_1 = \lambda$ and $\lambda_2 = \lambda'$. That is, the photon destroyed by a_{λ_1} must be the incident photon, and the one created by $a^\dagger_{\lambda_2}$ must be the scattered photon. Taking into account the other factors in the Fourier series, this product of operators corresponds to the product of polarization vectors $\hat{\boldsymbol{\epsilon}}_\lambda \cdot \hat{\boldsymbol{\epsilon}}^*_{\lambda'}$ and the product of phase factors $e^{i\mathbf{k}\cdot\mathbf{x}-i\mathbf{k}'\cdot\mathbf{x}}$. Similarly, the product of the creation operator times the annihilation operator $a^\dagger_{\lambda_1}a_{\lambda_2}$ contributes as long at $\lambda_1 = \lambda'$ and $\lambda_2 = \lambda$, and in this case the product of polarization vectors is $\hat{\boldsymbol{\epsilon}}^*_{\lambda'} \cdot \hat{\boldsymbol{\epsilon}}_\lambda$ and the product of phase factors is $e^{-i\mathbf{k}'\cdot\mathbf{x}+i\mathbf{k}\cdot\mathbf{x}}$.

Thus out of the double infinite series (20) for $\mathbf{A}^2$, only two terms contribute to the transition amplitude, and both have the same product of polarization vectors and the same phase factors. The contributions of these two terms are equal. It is now easy to do the photon part of the matrix element, leaving only an atomic matrix element. The result is

$$\langle n|H_2|i\rangle = 2 \times \frac{e^2}{2mc^2}\frac{2\pi\hbar c^2}{V}\frac{1}{\sqrt{\omega\omega'}}(\hat{\boldsymbol{\epsilon}}\cdot\hat{\boldsymbol{\epsilon}}'^*)\,\langle B|e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{x}}|A\rangle, \tag{21}$$

where the leading factor of 2 comes from the fact that we have two identical terms, and where we have made the abbreviations, $\hat{\boldsymbol{\epsilon}} = \hat{\boldsymbol{\epsilon}}_\lambda$, $\hat{\boldsymbol{\epsilon}}' = \hat{\boldsymbol{\epsilon}}_{\lambda'}$.

In the following we shall use the dipole approximation, in which $e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{x}} = 1$. As explained in Notes 41, this approximation is equivalent to $a/\lambda \ll 1$, where a is the size of the atom and λ is the wave length of the radiation. This is an excellent approximation for atoms at optical frequencies, where the ratio a/λ is less than 10^{-3}. This causes the atomic matrix element in Eq. (21) to become simply $\langle B|A\rangle = \delta_{BA}$. We see that the H_2-term only contributes to elastic scattering. Altogether, the matrix element becomes

$$\langle n|H_2|i\rangle = \Big(\frac{e^2\hbar}{m}\Big)\frac{2\pi}{V}\frac{1}{\sqrt{\omega\omega'}}(\hat{\boldsymbol{\epsilon}}\cdot\hat{\boldsymbol{\epsilon}}'^*)\,\delta_{BA}. \tag{22}$$

We have written the result in such a form that the first factor can be dropped if we are working in atomic units.