incorrect. The flaw will be corrected when we quantize the electromagnetic field in chapter seventeen, and then include interactions with atoms in chapter eighteen.

How do we interpret the delta functions in (15.21) and (15.22)? If our system has only discrete energy levels, these are a bit difficult to interpret, since a delta function is either zero or infinity. One solution in this case is to revert to forms like (15.20). We will find that if the energy conservation conditions are nearly satisfied, the rate is large but not infinite. In contrast, if they aren't well matched, the transitions do not grow with time. Roughly speaking, it is easy to show that the rate will be large provided the energy is matched with an approximate error $T\Delta E < \hbar$. This is yet another uncertainty relationship from quantum mechanics, one we will discuss later.

In other situations, the delta function is not really problematic. One that is commonly encountered is a situation where the perturbation is *not* strictly speaking harmonic, but rather a complicated function of many frequencies. In such circumstances, it is possible to break the perturbation into its Fourier components, and then add up (integrate) over all frequencies. The delta functions will pick out only that Fourier component with the right frequency to cause a transition. For example, in a thermal bath of electromagnetic radiation (black body radiation), there are electromagnetic waves of all frequencies present. An integration over all frequencies is necessary, in which case the delta function will make the computation easier.

Another common situation is when there are a continuum of final states $\left|\phi_F\right\rangle$; for example, if the initial state is a bound electron and the final state a free electron. Then the final state eigenstates might be labeled $\left|\mathbf{k}\right\rangle$, and have energy

$$H_0\left|\mathbf{k}\right\rangle = E_{\mathbf{k}}\left|\mathbf{k}\right\rangle = \frac{\hbar^2\mathbf{k}^2}{2m}\left|\mathbf{k}\right\rangle .$$

These states will be normalized, $\left\langle \mathbf{k}' \middle| \mathbf{k}\right\rangle = \delta^3\left(\mathbf{k}'-\mathbf{k}\right)$. We are not generally interested in the probability into a *particular* final state $\left|\mathbf{k}\right\rangle$, but rather the probability of the electron coming free, which will be given by

$$\Gamma\left(I \to \left|\mathbf{k}\right\rangle\right) = \int d^3\mathbf{k}\,\frac{2\pi}{\hbar}\left|W_{\mathbf{k}I}\right|^2 \delta\left(E_{\mathbf{k}} - E_I - \hbar\omega\right) = \frac{2\pi}{\hbar}\int d\Omega \int_0^\infty k^2 dk \left|W_{\mathbf{k}I}\right|^2 \delta\left(\frac{\hbar^2 k^2}{2m} - E_I - \hbar\omega\right)$$

$$= \frac{2\pi}{\hbar}\frac{mk^2}{\hbar^2 k}\int d\Omega \left|W_{\mathbf{k}I}\right|^2 = \frac{2\pi mk}{\hbar^3}\int d\Omega\left|W_{\mathbf{k}I}\right|^2 .$$

The matrix element $W_{\mathbf{k}I}$ will generally depend on direction. It is also possible to find the differential rate $d\Gamma/d\Omega$ simply by not performing the final angular integral.

E. Electromagnetic Waves and the Dipole Approximation

We consider now a special circumstance of considerable practical importance, the effect of electromagnetic plane waves on atoms. The full Hamiltonian will be given by (9.21), repeated here for clarity:

$$H = \sum_{j=1}^{N} \left\{ \frac{1}{2m} \left[\mathbf{P}_j + e\mathbf{A}\left(\mathbf{R}_j, t\right) \right]^2 - eU\left(\mathbf{R}_j, t\right) + \frac{e}{m} \mathbf{B}\left(\mathbf{R}_j, t\right) \cdot \mathbf{S}_j \right\} + V_a\left(\mathbf{R}_1, \mathbf{R}_2, \ldots\right),$$

where $V_a\left(\mathbf{R}_1, \mathbf{R}_2, \ldots\right)$ represents all the *internal* interactions of the atom, and **A** and **B** represent the effects of the *external* field, and (for this chapter and beyond) we have approximated $g = 2$ for the electron. We will now define the unperturbed Hamiltonian H_0 as

$$H_0 = \sum_{j=1}^{N} \frac{1}{2m} \mathbf{P}_j^2 + V_a\left(\mathbf{R}_1, \mathbf{R}_2, \ldots\right).$$

This Hamiltonian will have atomic eigenstates $\left|\phi_m\right\rangle$ with energy E_m. The perturbation will be all the remaining terms, but since we only want to keep only leading order in the electromagnetic fields, we will drop the $\mathbf{A}^2$ term. So we have[1]

$$W\left(t\right) = \sum_{j=1}^{N} \left\{ \frac{e}{m} \left[\mathbf{A}\left(\mathbf{R}_j, t\right) \cdot \mathbf{P}_j + \mathbf{B}\left(\mathbf{R}_j, t\right) \cdot \mathbf{S}_j \right] - eU\left(\mathbf{R}_j, t\right) \right\}. \qquad (15.23)$$

We now wish to include an electromagnetic wave. There is more than one way ("gauge choice") to write such a wave, which we will address more carefully in chapter seventeen, but for a specific choice of gauge ("Coulomb Gauge"), it can be written as

$$U\left(\mathbf{r}, t\right) = 0, \quad \mathbf{A}\left(\mathbf{r}, t\right) = A_0 \left(\boldsymbol{\varepsilon} e^{i\mathbf{k}\cdot\mathbf{r} - i\omega t} + \boldsymbol{\varepsilon}^* e^{-i\mathbf{k}\cdot\mathbf{r} + i\omega t} \right). \qquad (15.24)$$

where $\boldsymbol{\varepsilon}$ is a unit vector (the "polarization"[2]) normalized so that $\boldsymbol{\varepsilon} \cdot \boldsymbol{\varepsilon}^* = 1$, $\boldsymbol{\varepsilon} \cdot \mathbf{k} = 0$, and A_0 denotes the amplitude of the wave. The electric and magnetic fields are given by

$$\mathbf{E} = -\nabla U\left(\mathbf{r}, t\right) - \dot{\mathbf{A}}\left(\mathbf{r}, t\right) = iA_0\omega \left(\boldsymbol{\varepsilon} e^{i\mathbf{k}\cdot\mathbf{r} - i\omega t} - \boldsymbol{\varepsilon}^* e^{-i\mathbf{k}\cdot\mathbf{r} + i\omega t} \right),$$

$$\mathbf{B} = \nabla \times \mathbf{A} = iA_0 \left[\left(\mathbf{k} \times \boldsymbol{\varepsilon}\right) e^{i\mathbf{k}\cdot\mathbf{r} - i\omega t} - \left(\mathbf{k} \times \boldsymbol{\varepsilon}^*\right) e^{-i\mathbf{k}\cdot\mathbf{r} + i\omega t} \right].$$

Substituting into (15.22), we have

$$W\left(t\right) = \frac{e}{m} A_0 \sum_{j=1}^{N} \left\{ e^{i\mathbf{k}\cdot\mathbf{R}_j - i\omega t} \left[\boldsymbol{\varepsilon} \cdot \mathbf{P}_j + i\left(\mathbf{k} \times \boldsymbol{\varepsilon}\right) \cdot \mathbf{S}_j \right] + e^{-i\mathbf{k}\cdot\mathbf{R}_j + i\omega t} \left[\boldsymbol{\varepsilon}^* \cdot \mathbf{P}_j - i\left(\mathbf{k} \times \boldsymbol{\varepsilon}^*\right) \cdot \mathbf{S}_j \right] \right\}.$$

Comparison with (15.18) then tells us the perturbation with the time part factored out is

[1] Equation (15.23) seems to contain an error, since we commuted **A** with $\mathbf{P}_i$, not always a valid assumption. This assumption turns out to work in Coulomb gauge, since the choice of **A** given in (15.24) has no divergence.

[2] The polarization vector $\boldsymbol{\varepsilon}$ may be chosen real, yielding cosine dependence, or pure imaginary, yielding sine dependence. More complicated possibilities exist; for example, one may make one component real and another imaginary, resulting in circular polarization.

$$W = \frac{e}{m} A_0 \sum_{j=1}^{N} e^{i\mathbf{k}\cdot\mathbf{R}_j} \left[\boldsymbol{\varepsilon} \cdot \mathbf{P}_j + i\left(\mathbf{k} \times \boldsymbol{\varepsilon}\right) \cdot \mathbf{S}_j \right]. \tag{15.25}$$

We now want to spend a moment looking at (15.25). We will consider the case where we are using electromagnetic waves with energy $\hbar\omega$ comparable to the energy level splittings of an atom. These energy levels are typically of order $mc^2\alpha^2$, where $\alpha = \frac{1}{137}$ is the fine structure constant. A wave number *k* for such light will be of order $k \sim mc^2\alpha^2 / \hbar c = mc\alpha^2 / \hbar$. In contrast, the characteristic size of an atom will tend to be of order $a_0 = \hbar^2 / k_e e^2 m = \hbar / c\alpha m$. As a consequence, we have $\mathbf{k} \cdot \mathbf{R}_j \sim ka_0 \sim \alpha$. This is a small number, so to leading order, we simply treat it as zero, and drop the phase factor in (15.25). Similarly, if you compare the first and second terms in (15.25), the first term will be of order $\mathbf{P} \sim \hbar / a_0 = mc\alpha$, while the second will be of order $\mathbf{kS} \sim \hbar k \sim mc\alpha^2$. Hence we can ignore this as well. In summary, to leading order, our perturbation is

$$W_{E1} = \frac{e}{m} A_0 \sum_{j=1}^{N} \boldsymbol{\varepsilon} \cdot \mathbf{P}_j = \frac{e}{m} A_0 \boldsymbol{\varepsilon} \cdot \mathbf{P},$$

where **P** is just the sum of the momenta of all the electrons. This approximation is called the *electric dipole* approximation, and the *E*1 subscript just denotes this fact. The transition rate between two atomic states is then given by (15.21), assuming the final energy is greater than the initial energy.

$$\Gamma\left(I \to F\right) = \frac{2\pi A_0^2 e^2}{m^2 \hbar^2} \left| \boldsymbol{\varepsilon} \cdot \langle \phi_F | \mathbf{P} | \phi_I \rangle \right|^2 \delta\left(\omega_{FI} - \omega\right). \tag{15.26}$$

A couple of observations allow us to convert this into a more convenient form. The first is to note that the commutator of H_0 with $\mathbf{R} = \sum_i \mathbf{R}_i$ is given by

$$\left[H_0, \mathbf{R}\right] = \left[\sum_k \frac{1}{2m} \mathbf{P}_k^2 + V_a\left(\mathbf{R}_1, \mathbf{R}_2, \ldots\right), \sum_j \mathbf{R}_j \right] = \frac{1}{2m} \sum_{k,j} \left[\mathbf{P}_k^2, \mathbf{R}_j \right] = -\frac{i\hbar}{m} \sum_j \mathbf{P}_j = -\frac{i\hbar}{m} \mathbf{P}.$$

It follows that the matrix elements can be rewritten as

$$\langle \phi_F | \mathbf{P} | \phi_I \rangle = \frac{im}{\hbar} \langle \phi_F | \left[H_0, \mathbf{R}\right] | \phi_I \rangle = \frac{im}{\hbar} \langle \phi_F | \left(E_F \mathbf{R} - \mathbf{R} E_I\right) | \phi_I \rangle = im\omega_{FI} \langle \phi_F | \mathbf{R} | \phi_I \rangle. \tag{15.27}$$

It is also useful to rewrite the amplitude in terms of intensity. The intensity of a wave is given by the time-averaged magnitude of the Poynting vector,[1] which is given by

$$\langle \tilde{\mathbf{S}} \rangle = \frac{1}{\mu_0} \langle \mathbf{E} \times \mathbf{B} \rangle = \frac{A_0^2 \omega}{\mu_0} \left[\boldsymbol{\varepsilon} \times \left(\mathbf{k} \times \boldsymbol{\varepsilon}^*\right) + \boldsymbol{\varepsilon}^* \times \left(\mathbf{k} \times \boldsymbol{\varepsilon}\right) \right] = \frac{2A_0^2 \omega}{\mu_0} \mathbf{k}.$$

Recalling that for light we have $\omega = ck$, and finally remembering that $\mu_0 = 4\pi k_e / c^2$, we find that we can write the intensity $\mathcal{I}$, or power per unit area, as

[1] See, for example, p. 259, Jackson, *Classical Electrodynamics*, Third Edition (Wiley, 1999).

$$\mathcal{I} = \left|\left\langle \tilde{\mathbf{S}} \right\rangle\right| = \frac{2A_0^2\omega^2}{\mu_0 c} = \frac{A_0^2\omega^2 c}{2\pi k_e} . \tag{15.28}$$

Substituting (15.27) and (15.28) into (15.26) then yields

$$\Gamma\left(I \to F\right) = \frac{4\pi^2 k_e e^2 \omega_{FI}^2}{\hbar^2 c\omega^2} \mathcal{I} \left|\boldsymbol{\varepsilon} \cdot \left\langle \phi_F \left| \mathbf{R} \right| \phi_I \right\rangle\right|^2 \delta\left(\omega_{FI} - \omega\right).$$

The matrix element is often abbreviated $\mathbf{r}_{FI} \equiv \left\langle \phi_F \left| \mathbf{R} \right| \phi_I \right\rangle$ (the *electric dipole* matrix element). The delta function assures that $\omega_{FI} = \omega$, and we can write this more easily with the help of the fine structure constant $\alpha = k_e e^2 / \hbar c$, so this simplifies to

$$\Gamma\left(I \to F\right) = 4\pi^2 \alpha \hbar^{-1} \mathcal{I} \left|\boldsymbol{\varepsilon} \cdot \mathbf{r}_{FI}\right|^2 \delta\left(\omega_{FI} - \omega\right). \tag{15.29}$$

This yields an infinite rate if the frequency is appropriate. If the incoming wave has a *range* of frequencies, as all real sources do, then the intensity can be described as an intensity distribution, $\mathcal{I}\left(\omega\right)$ with units of power per unit area per unit angular frequency, so that[1]

$$\mathcal{I} = \int \mathcal{I}\left(\omega\right) d\omega .$$

We therefore modify (15.29) by including an appropriate integral, yielding

$$\Gamma\left(I \to F\right) = 4\pi^2 \alpha \hbar^{-1} \mathcal{I}\left(\omega_{FI}\right) \left|\boldsymbol{\varepsilon} \cdot \mathbf{r}_{FI}\right|^2 . \tag{15.30}$$

The rate will be identical for the reverse reaction.

Equation (15.30) is appropriate for an electromagnetic wave with known polarization vector $\boldsymbol{\varepsilon}$. If the polarization is random, we need to average over both polarizations perpendicular to the direction of the wave $\hat{\mathbf{n}}$. The easiest way to do this is to sum over all three potential polarizations and subtract the "missing" polarization $\hat{\mathbf{n}}$. The result is

$$\Gamma_{\text{unpol}} = 2\pi^2 \alpha \hbar^{-1} \mathcal{I}\left(\omega_{FI}\right) \left(\left|\mathbf{r}_{FI}\right|^2 - \left|\hat{\mathbf{n}} \cdot \mathbf{r}_{FI}\right|^2 \right).$$

If the incoming wave is coming in random direction, or if the atom is itself oriented in a random direction, we need to average over all angles, which yields

$$\Gamma_{\text{random}} = \tfrac{4}{3} \pi^2 \alpha \hbar^{-1} \mathcal{I}\left(\omega_{FI}\right) \left|\mathbf{r}_{FI}\right|^2 .$$

Let's try applying our formulas in a simple case. Consider a hydrogen atom in the ground state that is influenced by an electromagnetic field with sufficient frequency so that the electron can be ionized. The initial state is $\left|100\right\rangle$, but what shall we use for the final state? Far from the atom, the electron will be approximately a plane wave, but nearby the wave function is much more complicated. To simplify, assume the frequency

[1] A more likely experimental quantity than the intensity per unit angular frequency would be intensity per unit frequency $\mathcal{I}\left(f\right) = 2\pi \mathcal{I}\left(\omega\right)$ or intensity per unit wavelength $\mathcal{I}\left(\lambda\right) = \omega^2 \mathcal{I}\left(\omega\right) / 2\pi c$.

is *much* higher than is necessary to free an electron from hydrogen. In this case the final state will also be nearly a plane wave near the atom, since the kinetic energy is much greater than a typical binding energy. We need to calculate the matrix element $\mathbf{r}_{FI} = \langle \phi_F | \mathbf{R} | \phi_I \rangle = \langle \mathbf{k} | \mathbf{R} | 100 \rangle$, which with the help of (15.27) we can write as

$$\mathbf{r}_{FI} = \langle \mathbf{k} | \mathbf{R} | 100 \rangle = \frac{1}{im\omega_{FI}} \langle \mathbf{k} | \mathbf{P} | 100 \rangle = \frac{\hbar \mathbf{k}}{im\omega} \langle \mathbf{k} | 100 \rangle .$$

We now simply put in the specific form of the wave function and take its Fourier transform to give

$$\mathbf{r}_{FI} = \frac{\hbar \mathbf{k}}{im\omega} \frac{1}{(2\pi)^{3/2}} \int d^3 \mathbf{r} e^{-i\mathbf{k}\cdot\mathbf{r}} \frac{e^{-r/a_0}}{\sqrt{\pi a_0^3}} = \frac{\hbar \mathbf{k}}{im\omega} \frac{1}{\sqrt{2\pi\pi a_0^3}} \int_{-1}^{1} d\cos\theta \int_0^\infty r^2 dr e^{-r/a_0 - ikr\cos\theta}$$

$$= \frac{\sqrt{2}\hbar \mathbf{k}}{i\pi m\omega a_0^{3/2}} \int_{-1}^{1} \frac{d\cos\theta}{\left(a_0^{-1} + ik\cos\theta\right)^3} = \frac{\hbar \mathbf{k} \left(a_0^{-1} + ik\cos\theta\right)^{-2}}{\pi\sqrt{2} mk\omega a_0^{3/2}} \Bigg|_{\cos\theta=-1}^{\cos\theta=1}$$

$$= \frac{\hbar \mathbf{k}}{\pi\sqrt{2} mk\omega a_0^{3/2}} \left[\frac{1}{\left(a_0^{-1} + ik\right)^2} - \frac{1}{\left(a_0^{-1} - ik\right)^2} \right] = -\frac{2\sqrt{2} i\hbar \mathbf{k} a_0^{3/2}}{\pi m\omega \left(1 + a_0^2 k^2\right)^2} .$$

Substituting this into (15.29), we have

$$\Gamma(1s \to \mathbf{k}) = 4\pi^2 \alpha \hbar^{-1} \mathcal{I} \left(\frac{8\hbar^2 a_0^3}{\pi^2 m^2 \omega^2} \right) \left(1 + a_0^2 k^2\right)^{-4} |\boldsymbol{\varepsilon} \cdot \mathbf{k}|^2 \, \delta(\omega_{FI} - \omega)$$

$$= 32\alpha \mathcal{I} a_0^3 \hbar^2 |\boldsymbol{\varepsilon} \cdot \mathbf{k}|^2 \, m^{-2} \omega^{-2} \left(1 + a_0^2 k^2\right)^{-4} \delta\left(\frac{\hbar^2 k^2}{2m} - E_I - \hbar\omega \right) .$$

The dot product is just $\boldsymbol{\varepsilon} \cdot \mathbf{k} = k\cos\theta$ where θ is the angle between the polarization of the light and the direction of the final electron. We would then integrate this over all possible final wave numbers **k** to yield

$$\Gamma(1s \to \mathbf{k}) = \frac{32\alpha \mathcal{I} a_0^3 \hbar^2 k^2}{m^2 \omega^2 \left(1 + a_0^2 k^2\right)^4} \int_0^\infty \delta\left[\frac{\hbar^2 k^2}{2m} - E_I - \hbar\omega \right] k^2 dk \int \cos^2\theta \, d\Omega ,$$

$$\frac{d\Gamma}{d\Omega} = \frac{32\alpha \mathcal{I} a_0^3 k^3}{m\omega^2 \left(1 + a_0^2 k^2\right)^4} \cos^2\theta ,$$

where the final wave number k is defined by $\hbar^2 k^2 / 2m = E_I + \hbar\omega$. The final angular integral, if desired, yields an additional factor $\int d\Omega \cos^2\theta = \frac{4}{3}\pi$.

F. Beyond the Dipole Approximation

Suppose the dipole moment $\mathbf{r}_{FI} = \langle \phi_F | \mathbf{R} | \phi_I \rangle$ between an initial and final state vanishes. After all, the matrix element will generally vanish unless $l_F = l_I \pm 1$, so this will commonly be the case. Does this mean that the decay does not occur? No, it only means that its rate will be suppressed. Let us expand out the expression (15.25), but this time keeping more than just the leading term. We have

$$W = \frac{e}{m} A_0 \sum_{j=1}^{N} \left[\boldsymbol{\varepsilon} \cdot \mathbf{P}_j + i \left(\mathbf{k} \cdot \mathbf{R}_j \right) \left(\boldsymbol{\varepsilon} \cdot \mathbf{P}_j \right) + i \left(\mathbf{k} \times \boldsymbol{\varepsilon} \right) \cdot \mathbf{S}_j \right]. \tag{15.31}$$

The leading term is responsible for electric dipole transitions. The middle term can be rewritten, with the help of some fancy vector identities, in the form

$$\left(\mathbf{k} \cdot \mathbf{R}_j \right) \left(\boldsymbol{\varepsilon} \cdot \mathbf{P}_j \right) = \tfrac{1}{2} \left[\left(\mathbf{k} \cdot \mathbf{R}_j \right) \left(\boldsymbol{\varepsilon} \cdot \mathbf{P}_j \right) + \left(\mathbf{k} \cdot \mathbf{P}_j \right) \left(\boldsymbol{\varepsilon} \cdot \mathbf{R}_j \right) \right] + \tfrac{1}{2} \left(\mathbf{k} \times \boldsymbol{\varepsilon} \right) \cdot \left(\mathbf{R}_j \times \mathbf{P}_j \right).$$

The latter term contains the angular momentum $\mathbf{L}_j$ of the j'th electron, and it is not hard to show that the first term can be written as a commutator, in a manner similar to before

$$\left(\mathbf{k} \cdot \mathbf{R}_j \right) \left(\boldsymbol{\varepsilon} \cdot \mathbf{P}_j \right) + \left(\mathbf{k} \cdot \mathbf{P}_j \right) \left(\boldsymbol{\varepsilon} \cdot \mathbf{R}_j \right) = \frac{im}{\hbar} \left[H_0, \left(\mathbf{k} \cdot \mathbf{R}_j \right) \left(\boldsymbol{\varepsilon} \cdot \mathbf{R}_j \right) \right].$$

With a bit of work, we then find the matrix elements are given by

$$\langle \phi_F | W | \phi_I \rangle = \frac{iA_0 e}{m} \langle \phi_F | \sum_{j=1}^{N} \left\{ \frac{im}{2\hbar} \left[H_0, \left(\mathbf{k} \cdot \mathbf{R}_j \right) \left(\boldsymbol{\varepsilon} \cdot \mathbf{R}_j \right) \right] + \tfrac{1}{2} \left(\mathbf{k} \times \boldsymbol{\varepsilon} \right) \cdot \mathbf{L}_j + \left(\mathbf{k} \times \boldsymbol{\varepsilon} \right) \cdot \mathbf{S}_j \right\} | \phi_I \rangle,$$

$$W_{FI} = -\tfrac{1}{2} \omega_{FI} A_0 e \sum_{j=1}^{N} \langle \phi_F | \left(\mathbf{k} \cdot \mathbf{R}_j \right) \left(\boldsymbol{\varepsilon} \cdot \mathbf{R}_j \right) | \phi_I \rangle + \frac{iA_0 e}{m} \left(\mathbf{k} \times \boldsymbol{\varepsilon} \right) \cdot \langle \phi_F | \left(\tfrac{1}{2} \mathbf{L} + \mathbf{S} \right) | \phi_I \rangle.$$

The first term is referred to as the *electric quadrupole* term, and the second is the *magnetic dipole* term. Both terms commute with parity, unlike the electric dipole term, and therefore they can only connect states with the same parity. Hence the states connected by these terms are always different from the ones connected by the electric dipole term, and there is no interference between the two. The electric quadrupole term is a rank two spherical tensor operator; as such it changes l by either zero or two, but cannot connect two $l = 0$ states. The magnetic dipole term commutes with H_0, assuming we ignore spin-orbit coupling, hyperfine splitting, and external magnetic fields. Hence it can only cause transitions for states that are split by these smaller effects.

These expressions can then be used to compute rates, in a manner similar to the electric dipole moment. For example, the quadrupole contribution to decay is given by

$$\Gamma \left(I \to F \right) = \pi^2 \alpha \hbar^{-1} \mathcal{I} \left(\omega_{FI} \right) \left| \sum_{j=1}^{N} \langle \phi_F | \left(\mathbf{k} \cdot \mathbf{R}_j \right) \left(\boldsymbol{\varepsilon} \cdot \mathbf{R}_j \right) | \phi_I \rangle \right|^2 .$$

This is suppressed compared to the electric dipole rate by a factor $\left(\mathbf{k} \cdot \mathbf{R} \right)^2$, typically of order α^2.

G. Time-dependent perturbation theory with a constant perturbation

The last type of perturbation we want to consider is one that is constant in time, $W(t) = W$. It may seem odd to use time-dependent perturbation theory in such a circumstance, but in fact, it is often a very good way of thinking about things. For example, if I scatter a particle off of a potential, we intuitively imagine a particle approaching the potential (initially in a plane wave), interacting with the potential (the interaction) and then leaving the potential again (a plane wave). Although the potential is *in fact* always constant, it is easier to think of it as a temporary perturbation.

Our starting point will once again be (15.14), but we will make a couple of modifications. First of all, we ultimately want to consider the perturbation as constant, not having time dependence at all, so that it is always on and always will be on. For this reason, we will change the integration to run from $-\frac{1}{2}T$ to $\frac{1}{2}T$. Eq. (15.14) then will look like

$$S_{FI} = \delta_{FI} + \frac{W_{FI}}{i\hbar}\int_{-\frac{1}{2}T}^{\frac{1}{2}T} dt\, e^{i\omega_{FI}t} + \sum_m \frac{W_{Fm}W_{mI}}{(i\hbar)^2}\int_{-\frac{1}{2}T}^{\frac{1}{2}T} dt \int_{-\frac{1}{2}T}^{\frac{1}{2}T} dt'\,\theta(t-t')\,e^{i\omega_{Fm}t}e^{i\omega_{mI}t'}$$

$$+\sum_m\sum_n \frac{W_{Fm}W_{mn}W_{nI}}{(i\hbar)^3}\int_{-\frac{1}{2}T}^{\frac{1}{2}T} dt \int_{-\frac{1}{2}T}^{\frac{1}{2}T} dt' \int_{-\frac{1}{2}T}^{\frac{1}{2}T} dt''\,\theta(t-t')\,\theta(t'-t'')\,e^{i\omega_{Fm}t}e^{i\omega_{mn}t'}e^{i\omega_{nI}t''} + \cdots, \quad (15.32)$$

where we have used the *Heaviside function*, defined by

$$\theta(\tau) \equiv \begin{cases} 1 & \text{if } \tau > 0, \\ 0 & \text{if } \tau < 0. \end{cases}$$

We now wish to prove the identity

$$\theta(\tau) = \lim_{\varepsilon\to 0^+}\frac{1}{2\pi i}\int_{-\infty}^{\infty}\frac{e^{i\omega\tau}\,d\omega}{\omega - i\varepsilon}. \quad (15.33)$$

This integral will be evaluated by the method of contour integration.

Contour integration is a method that can be used to perform integrals in the complex plane. As defined, the integral in (15.33) runs from minus infinity to infinity along the real axis. The first step of performing a contour integral is to "close" the contour: to add an additional path from infinity back to minus infinity to make a complete loop. The trick is to choose that path such that it contributes negligibly to the integral. Since we are going to be wandering into values of ω that are imaginary, our goal is to pick values of ω such that $e^{i\omega\tau}$ will be very small. This will be the case provided

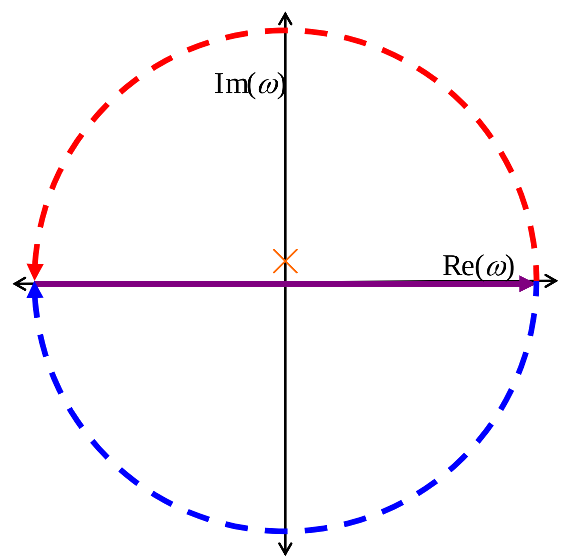

Figure 15-6: Contours for performing the integral (15.33). To the initial path (purple line), we add a half-circle at infinity in the upper half plane for $\tau > 0$ (red semi-circle) or the lower half plane for $\tau < 0$ (blue semi-circle). The orange X is the pole at $\omega = i\varepsilon$.

$i\omega\tau$ has a large negative real part. If $\tau > 0$, this is simply achieved by forcing $\operatorname{Im}(\omega) > 0$ (the "upper half plane") whereas if $\tau < 0$, we force $\operatorname{Im}(\omega) < 0$ (the "lower half plane"). We can therefore add a half loop "at infinity" to make the whole integral a closed loop, as illustrated in Fig. 15-6.

We now employ the magic of contour integration, which says that the result of an integral is independent of the path chosen, provided we do not cross the pole. We can therefore shrink, in each case, the integral to a tiny circle, enclosing the pole in the case $\tau > 0$, and enclosing nothing for $\tau < 0$, as illustrated in Fig. 15-7. While we are at it we can take the limit $\varepsilon \to 0$, which places the pole at the origin. We now have

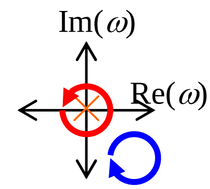

Figure 15-7: The contours after they have been shrunk. The pole has been moved to $\omega = 0$. For $\tau > 0$, the contour contains the pole (red curve), and the integral is non-zero, for $\tau < 0$, the contour can be shrunk to zero (blue curve), and the integral vanishes.

$$\lim_{\varepsilon\to 0^+} \frac{1}{2\pi i}\int_{-\infty}^{\infty} \frac{e^{i\omega\tau} d\omega}{\omega - i\varepsilon} = \frac{1}{2\pi i}\cdot\begin{cases} \oint e^{i\omega\tau} d\omega/\omega & \text{if } \tau > 0, \\ \oint e^{i\omega\tau} d\omega/\omega & \text{if } \tau < 0. \end{cases}$$

The loop for $\tau < 0$ can be shrunk to zero with impunity, and we can locate it well away from the pole if we wish, so the integral vanishes. For $\tau > 0$, we shrink it to a tiny circle of radius δ. In the limit $\delta \to 0$ we have $\omega \approx 0$, and we can approximate $e^{i\omega\tau} = 1$. However, we dare not make this approximation in the denominator. We parameterize the tiny circle around the origin by an angle ϕ and let $\omega = \delta e^{i\phi}$, where ϕ runs from 0 to 2π. Then we have, for $\tau > 0$,

$$\lim_{\varepsilon\to 0^+} \frac{1}{2\pi i}\int_{-\infty}^{\infty} \frac{e^{i\omega\tau} d\omega}{\omega - i\varepsilon} = \frac{1}{2\pi i}\int_0^{2\pi} \frac{d\left(\delta e^{i\phi}\right)}{\delta e^{i\phi}} = \frac{1}{2\pi i}\int_0^{2\pi} i\,d\phi = 1,$$

while it vanishes for $\tau < 0$, which proves (15.33)

We now wish to use this identity to simplify (15.32). We replace each of the Heaviside functions with the messy integral (15.33), which results in

$$\begin{aligned} S_{FI} = \delta_{FI} &+ \frac{W_{FI}}{i\hbar}\int_{-\frac{1}{2}T}^{\frac{1}{2}T} dt\, e^{i\omega_{FI}t} + \lim_{\varepsilon\to 0^+}\left[\sum_m \frac{W_{Fm}W_{mI}}{(i\hbar)^2}\int_{-\frac{1}{2}T}^{\frac{1}{2}T} dt \int_{-\frac{1}{2}T}^{\frac{1}{2}T} dt'\, e^{i\omega_{Fm}t} e^{i\omega_{mI}t'} \int_{-\infty}^{\infty} \frac{e^{i\omega(t-t')}d\omega}{2\pi i(\omega - i\varepsilon)}\right. \\ &\left. + \sum_m\sum_n \frac{W_{Fm}W_{mn}W_{nI}}{(i\hbar)^3}\int_{-\frac{1}{2}T}^{\frac{1}{2}T} dt \int_{-\frac{1}{2}T}^{\frac{1}{2}T} dt' \int_{-\frac{1}{2}T}^{\frac{1}{2}T} dt''\, e^{i\omega_{Fm}t} e^{i\omega_{mn}t'} e^{i\omega_{nI}t''} \int_{-\infty}^{\infty} \frac{e^{i\omega(t-t')}d\omega}{2\pi i(\omega - i\varepsilon)} \int_{-\infty}^{\infty} \frac{e^{i\omega'(t'-t'')}d\omega'}{2\pi i(\omega' - i\varepsilon)} + \cdots \right], \end{aligned}$$

We now proceed to perform all but one of the time integrals. We will do so simply by working in the infinite time limit, so that the integrals turn into trivial expressions like $\int_{-\infty}^{\infty} e^{i(\omega_{mI}-\omega)t'} dt' = 2\pi\delta(\omega_{mI} - \omega)$. Using this on all the integrals except for dt, we obtain

$$S_{FI} = \delta_{FI} + \frac{W_{FI}}{i\hbar}\int_{-\frac{1}{2}T}^{\frac{1}{2}T} dt\, e^{i\omega_{FI}t} + \lim_{\varepsilon\to 0^+}\left\{\sum_m \frac{W_{Fm}W_{mI}}{(i\hbar)^2}\int_{-\frac{1}{2}T}^{\frac{1}{2}T} e^{i\omega t}dt \int_{-\infty}^{\infty} e^{i\omega_{Fm}t}\,\frac{\delta(\omega-\omega_{mI})\,d\omega}{i(\omega - i\varepsilon)}\right.$$

$$\left. + \sum_m\sum_n \frac{W_{Fm}W_{mn}W_{nI}}{(i\hbar)^3}\int_{-\frac{1}{2}T}^{\frac{1}{2}T} e^{i\omega_{Fm}t}dt \int_{-\infty}^{\infty}\frac{e^{i\omega t}\delta(\omega_{mn}+\omega'-\omega)\,d\omega}{i(\omega-i\varepsilon)}\int_{-\infty}^{\infty}\frac{\delta(\omega_{nI}-\omega')\,d\omega'}{i(\omega'-i\varepsilon)} + \cdots\right\}.$$

We now use the Dirac delta functions to do all the ω-integrations.

$$S_{FI} = \delta_{FI} + \frac{W_{FI}}{i\hbar}\int_{-\frac{1}{2}T}^{\frac{1}{2}T} dt\, e^{i\omega_{FI}t} + \lim_{\varepsilon\to 0^+}\left\{\sum_m \frac{W_{Fm}W_{mI}}{(i\hbar)^2\, i(\omega_{mI}-i\varepsilon)}\int_{-\frac{1}{2}T}^{\frac{1}{2}T} e^{i(\omega_{Fm}+\omega_{mI})t}dt\right.$$

$$\left. + \sum_m\sum_n \frac{W_{Fm}W_{mn}W_{nI}}{(i\hbar)^3\, i(\omega_{nI}-i\varepsilon)\, i(\omega_{mn}+\omega_{nI}-i\varepsilon)}\int_{-\frac{1}{2}T}^{\frac{1}{2}T} e^{i(\omega_{Fm}+\omega_{mn}+\omega_{nI})t}dt\right\} + \cdots.$$

We rewrite $\hbar\omega_{ij} = E_i - E_j$, and write this in the form

$$S_{FI} = \delta_{FI} + \frac{1}{i\hbar}\int_{-\frac{1}{2}T}^{\frac{1}{2}T} dt\, e^{i\omega_{FI}t}\left\{W_{FI} + \lim_{\varepsilon\to 0^+}\left[\sum_m \frac{W_{Fm}W_{mI}}{(E_I - E_m + i\varepsilon\hbar)}\right.\right.$$

$$\left.\left. + \sum_m\sum_n \frac{W_{Fm}W_{mn}W_{nI}}{(E_I - E_n + i\varepsilon\hbar)(E_I - E_m + i\varepsilon\hbar)} + \cdots\right]\right\}$$

We now define the *transition matrix* $\mathcal{T}_{FI}$ as

$$\mathcal{T}_{FI} \equiv W_{FI} + \lim_{\varepsilon\to 0^+}\left[\sum_m \frac{W_{Fm}W_{mI}}{(E_I - E_m + i\varepsilon)} + \sum_m\sum_n \frac{W_{Fm}W_{mn}W_{nI}}{(E_I - E_n + i\varepsilon)(E_I - E_m + i\varepsilon)} + \cdots\right], \tag{15.34}$$

where we have changed $\varepsilon\hbar \to \varepsilon$ since we are taking the limit $\varepsilon \to 0^+$ anyway. The pattern is clear, at each order in perturbation theory, we get one more factor of *W* in the numerator, summed over all possible intermediate states, while in the denominator we always get factors of the initial energy minus any intermediate energy, together with an $i\varepsilon$ term that will bear some discussion later. Then our scattering matrix will be given by

$$S_{FI} = \delta_{FI} + \frac{1}{i\hbar}\int_{-\frac{1}{2}T}^{\frac{1}{2}T} \mathcal{T}_{FI}\, dt\, e^{i\omega_{FI}t} = \delta_{FI} + \frac{1}{i\hbar}\mathcal{T}_{FI}\,\frac{2\sin\left(\frac{1}{2}\omega_{FI}T\right)}{\omega_{FI}}.$$

If the final state is different from our initial state, we ignore the first term and find

$$P(I\to F) = \frac{4}{\hbar^2}\left|\mathcal{T}_{FI}\right|^2\frac{\sin^2\left(\frac{1}{2}\omega_{FI}T\right)}{\omega_{FI}^2}.$$

This expression was encountered around (15.20), where we argued that in the limit of large *T*, it becomes a delta function. Using our results there, we find

$$P\left(I \to F\right) = 2\pi\hbar^{-2}\left|\mathcal{T}_{FI}\right|^2 T\delta\left(\omega_{FI}\right).$$

We again let the rate be the probability divided by time, and conventionally place one factor of $\hbar$ inside the delta-function, to obtain Fermi's Golden Rule

$$\Gamma\left(I \to F\right) = 2\pi\hbar^{-1}\left|\mathcal{T}_{FI}\right|^2 \delta\left(E_F - E_I\right). \tag{15.35}$$

This, together with (15.34), allows us to calculate transition rates to arbitrary order.

To understand how to apply Fermi's Golden rule in a simple situation, consider a plane wave scattering off of a weak potential. We will let the unperturbed Hamiltonian be the free particle Hamiltonian, $H_0 = \mathbf{P}^2/2m$, and the potential V be the perturbation. Then our eigenstates of H_0 will be plane waves, and to leading order, $\mathcal{T}_{FI}$ will be

$$\mathcal{T}_{FI} = V_{FI} = \left\langle \mathbf{k}_F \left| V\left(\mathbf{R}\right) \right| \mathbf{k}_I \right\rangle = \int \frac{d^3\mathbf{r}}{\left(2\pi\right)^3} e^{-i\mathbf{k}_F\cdot\mathbf{r}} V\left(\mathbf{r}\right) e^{i\mathbf{k}_I\cdot\mathbf{r}}$$

The rate (15.35) is then given by

$$\Gamma\left(I \to F\right) = \frac{1}{\left(2\pi\right)^5\hbar}\left|\int d^3\mathbf{r}e^{-i\left(\mathbf{k}_F - \mathbf{k}_I\right)\cdot\mathbf{r}} V\left(\mathbf{r}\right)\right|^2 \delta\left[\frac{\hbar^2}{2m}\left(k_F^2 - k_I^2\right)\right].$$

There are two problems with this formula: first, neither our initial nor our final state plane waves are normalized properly, and second, the delta function is a bit difficult to interpret. We can get rid of one and one-half of these problems by "summing" over the final state momenta, which then becomes an integral.

$$\Gamma\left(I \to F\right) = \frac{1}{\left(2\pi\right)^5\hbar}\int d^3\mathbf{k}_F\left|\int d^3\mathbf{r}e^{-i\left(\mathbf{k}_F - \mathbf{k}_I\right)\cdot\mathbf{r}} V\left(\mathbf{r}\right)\right|^2 \delta\left[\frac{\hbar^2}{2m}\left(k_F^2 - k_I^2\right)\right]$$

$$= \frac{1}{\left(2\pi\right)^5\hbar}\int_0^\infty k_F^2 dk_F \delta\left[\frac{\hbar^2}{2m}\left(k_F^2 - k_I^2\right)\right]\int d\Omega\left|\int d^3\mathbf{r}e^{-i\left(\mathbf{k}_F - \mathbf{k}_I\right)\cdot\mathbf{r}} V\left(\mathbf{r}\right)\right|^2,$$

$$\frac{d\Gamma}{d\Omega} = \frac{mk}{\left(2\pi\right)^5\hbar^3}\left|\int d^3\mathbf{r}e^{-i\left(\mathbf{k}_F - \mathbf{k}_I\right)\cdot\mathbf{r}} V\left(\mathbf{r}\right)\right|^2. \tag{15.36}$$

The one remaining difficulty is that the incident plane wave cannot be normalized. In a manner similar to last chapter, we note that the incident wave has a probability density $\left|\psi\right|^2 = \left(2\pi\right)^{-3}$ and is moving with classical velocity $\hbar k/m$, implying a flux of $\Phi = \left(\hbar k/m\right)\left(2\pi\right)^{-3}$. This allows us to convert (15.36) into a differential cross-section.

$$\frac{d\sigma}{d\Omega} = \frac{1}{\Phi}\frac{d\Gamma}{d\Omega} = \frac{m^2}{4\pi^2\hbar^4}\left|\int d^3\mathbf{r}e^{-i\left(\mathbf{k}_F - \mathbf{k}_I\right)\cdot\mathbf{r}} V\left(\mathbf{r}\right)\right|^2.$$

This is none other than the first Born approximation, eq. (14.19).

Problems for Chapter 15

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1. An isolated tritium (hydrogen) atom ^{3}H has its electron in the ground state when it suddenly radioactively decays to ^{3}He, (helium) but the nucleus stays in the same place (no recoil). What is the probability that the atoms remains in the ground state? What is the probability that it goes into each of the *n* = 2 states $\left|2lm\right\rangle$?

2. A neutral boron atom has a total angular momentum *l* = 1 and spin *s* = ½. In the absence of a magnetic field, the lowest energy states might be listed as $\left|l,s,j,m_j\right\rangle = \left|1,\tfrac{1}{2},j,m_j\right\rangle$, with the $j=\tfrac{3}{2}$ state having higher energy. The atom is placed in a region of space where a magnetic field is being turned on in the +z direction. At first, the spin-orbit coupling dominates, but at late times the magnetic interactions dominate.
   (a) Which of the nine operators **L**, **S** and **J** will commute with the Hamiltonian at all times? Note that the state must remain an eigenstate of this operator at all times.
   (b) At strong magnetic fields, the states are dominated by the magnetic field. The eigenstates are approximately $\left|l,s,m_l,m_s\right\rangle = \left|1,\tfrac{1}{2},m_l,m_s\right\rangle$. For each possible value of $m_j = m_l + m_s$, deduce which state has the lower energy. Atoms in strong magnetic fields are discussed in chapter 9, section E.
   (c) If we start with a particular value of $\left|l,s,j,m_j\right\rangle$ (six cases), calculate which states $\left|l,s,m_l,m_s\right\rangle$ it might evolve into, assuming the magnetic field increases (i) adiabatically (slowly) or (ii) suddenly. When relevant, give the corresponding probabilities. The relevant Clebsch-Gordan coefficients are given in eq. (8.18).

3. A particle of mass *m* is initially in the ground state of a harmonic oscillator with frequency ω. At time *t* = 0, a perturbation is suddenly turned on of the form $W(t) = AXe^{-\lambda t}$. At late times ($t\to\infty$), the quantum state is measured again.
   (a) Calculate, to second order in *A*, the amplitude S_{n0} that it ends up in the state $\left|n\right\rangle$, for all *n* (most of them will be zero).
   (b) Calculate, to at least second order, the probability that it ends up in the state $\left|n\right\rangle$. Check that the sum of the probabilities is 1, to second order in *A*.

4. A particle of mass *m* is in the ground state $\left|1\right\rangle$ of an infinite square well with allowed region $0 < X < a$. To this potential is added a harmonic perturbation $W(t) = AX\cos(\omega t)$, where *A* is small.
   (a) Calculate the transition rate $\Gamma(1\to n)$ for a transition to another level. Don't let the presence of a delta function bother you. What angular frequency ω is necessary to make the transition occur to level *n* = 2?
   (b) Now, instead of keeping a constant frequency, the frequency is tuned continuously, so that at *t* = 0 the frequency is 0, and it rises linearly so that at *t* = *T*

it has increased to the value $\omega(T) = 2\pi^2\hbar/ma^2$. The tuning is so slow that at any given time, we may treat it as a harmonic source. Argue that only the *n* = 2 state can become populated (to leading order in *A*). Calculate the probability of a transition using $P(1\to 2) = \int_0^T \Gamma(1\to 2)\,dt$.

5. A hydrogen atom is in the 1s ground state while being bathed in light of sufficient frequency to excite it to the *n* = 2 states. The light is traveling in the +*z* direction and has circular polarization, $\boldsymbol{\varepsilon} = \frac{1}{\sqrt{2}}(\hat{\mathbf{x}} + i\hat{\mathbf{y}})$.
   (a) Calculate all relevant dipole moments $\mathbf{r}_{FI}$ for final states $|2lm\rangle$.
   (b) Find a formula for the rate at which the atom makes this transition.
   (c) What is the wavelength required for this transition? Assume at this wavelength the power is $\mathcal{I}(\lambda) = 100\ \text{W/m}^2/\text{nm}$. Find the rate at which the atom converts. (Note the footnote on p. 280)

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6. A hydrogen atom is in interstellar space in the 1s state, but not in the true ground state (*F* = 0), but rather in the hyperfine excited state (*F*=1), specifically in the state $|\phi_I\rangle = |n,l,j,F,m_F\rangle = |1,0,\frac{1}{2},1,0\rangle$. It is going to transition to the true ground state $|\phi_F\rangle = |n,l,j,F,m_F\rangle = |1,0,\frac{1}{2},0,0\rangle$ via a magnetic dipole interaction.
   (a) Write out the initial and final states in terms of the explicit spin states of the electron and proton $|\pm,\pm\rangle$. Find all non-zero components of the matrix $\langle\phi_F|\mathbf{S}|\phi_I\rangle$, where S is the electron spin operator.
   (b) Show that the rate for this transition for a wave going in a specific direction with a definite polarization is given by $\Gamma = 4\pi^2 m^{-2}\omega^{-2}\alpha\mathcal{I}\left|(\mathbf{k}\times\boldsymbol{\varepsilon})\cdot\mathbf{S}_{FI}\right|^2 \delta(E_F - E_I + \hbar\omega)$.
   (c) Show that for a wave going in a random direction with random polarization, this simplifies to $\Gamma(I\to F) = \frac{4}{3}\pi^2\alpha m^{-2}c^{-2}\mathcal{I}\left|\mathbf{S}_{FI}\right|^2 \delta(E_f - E_i + \hbar\omega)$.
   (d) For low frequencies, the cosmic microwave background intensity is $\mathcal{I}(\omega) = k_B T\omega^2/\pi^2 c^2$ where k_B is Boltzman's constant and *T* is the temperature. Integrate the flipping rate over frequency. Find the mean time Γ^{-1} for a hydrogen atom to reverse itself in a background temperature *T* = 2.73 K for $\omega_{FI} = -2\pi(1.420\ \text{GHz})$.

7. A spin ½ particle of mass *m* lies in a one-dimensional spin-dependant potential $H_0 = P^2/2m + \frac{1}{2}m\omega^2 X^2 |+\rangle\langle+|$. The potential only affects particles in a spin-up state.
   (a) Find the discrete energy eigenstates for spin-up ($|+,i\rangle$) and the continuum energy eigenstates for spin-down ($|-,\beta\rangle$). Also, identify their energies.
   (b) At *t* = 0, a spin-dependant perturbation of the form $V = \hbar\gamma\sigma_x$, where σ_x is a Pauli matrix, is turned on. Calculate the rate Γ at which the spin-up ground state "decays" to a continuum state.

XVI. The Dirac Equation

We turn our attention to a discussion of a relativistic theory of the electron, the Dirac Equation. Although the approach we use is now considered obsolete, it does provide important insights into relativistic quantum mechanics, and ultimately it was an important step on the way to a modern theory of particle physics.

As a first step, consider the procedure we used to produce the free particle Hamiltonian. We started with the non-relativistic formula for energy, namely, $E = \mathbf{p}^2/2m$, multiplied by a wave function $\Psi(\mathbf{r},t)$ and then made the substitutions $E \to i\hbar\,\partial/\partial t$ and promoted $\mathbf{p}$ to an operator, $\mathbf{p} \to \mathbf{P}$ to produce the free particle Schrödinger equation,

$$i\hbar\frac{\partial}{\partial t}\Psi = \frac{1}{2m}\mathbf{P}^2\Psi .$$

Now, the corresponding relativistic equation for energy is $E^2 = c^2\mathbf{p}^2 + m^2c^4$. It is then easy to derive a corresponding Schrödinger-like equation by the same prescription:

$$\left(i\hbar\frac{\partial}{\partial t}\right)^2\Psi = c^2\mathbf{P}^2\Psi + m^2c^4\Psi , \qquad (16.1)$$

the Klein-Gordon equation. The problem with (16.1) is that it is second order in time. As such, to predict the wave function $\Psi(\mathbf{r},t)$ at arbitrary time, we would need to know not just the initial wave-function $\Psi(\mathbf{r},0)$, but also its first derivative $\dot{\Psi}(\mathbf{r},0)$, contradicting the first postulate of quantum mechanics. We need to find a way to convert (16.1) into a first order differential equation for the wave function.

A. The Dirac Equation

As inspiration for finding the correct equation, let's back up a bit, and look at our formula for the Hamiltonian in the presence of electromagnetic fields, eq. (9.20), but we will approximate $g = 2$. The Schrödinger equation is

$$i\hbar\frac{\partial}{\partial t}\Psi = \frac{\boldsymbol{\pi}^2}{2m}\Psi - eU\Psi + \frac{e\hbar}{2m}\mathbf{B}\cdot\boldsymbol{\sigma}\Psi . \qquad (16.2)$$

where we have used the explicit form of the spin operator $\mathbf{S} = \frac{1}{2}\hbar\boldsymbol{\sigma}$. We wish to rewrite this in a simpler form. We start with identity (7.18) for the Pauli matrices. With the help of (9.16c), it is then not hard to show

$$(\boldsymbol{\sigma}\cdot\boldsymbol{\pi})^2 = \boldsymbol{\pi}^2 + i\sigma_x\left[\pi_y,\pi_z\right] + i\sigma_y\left[\pi_z,\pi_x\right] + i\sigma_z\left[\pi_x,\pi_y\right] = \boldsymbol{\pi}^2 + e\hbar\boldsymbol{\sigma}\cdot\mathbf{B} .$$

This allows us to write (16.2) in the alternate form

$$i\hbar\frac{\partial}{\partial t}\Psi = \frac{1}{2m}(\boldsymbol{\sigma}\cdot\boldsymbol{\pi})^2\Psi - eU\Psi . \qquad (16.3)$$

Let us, at least temporarily, drop the electromagnetic interactions, in which case (16.3) takes the simpler form

$$i\hbar \frac{\partial}{\partial t}\Psi = \frac{1}{2m}\left(\boldsymbol{\sigma}\cdot\mathbf{P}\right)^2 \Psi\,. \tag{16.4}$$

This is, of course, identical with the standard form $H = \mathbf{P}^2/2m$, but the presence of spin will ultimately help us develop the Dirac equation.

Inspired by (16.4), let us consider rewriting (16.1) in the form

$$\left(i\hbar \frac{\partial}{\partial t}\right)^2 \phi = c^2\left(\boldsymbol{\sigma}\cdot\mathbf{P}\right)^2 \phi + m^2c^4\phi\,,$$

where we have written the wave function as ϕ for reasons that will soon become apparent. Note that ϕ has two components, as it must for this expression to have any meaning. We now shift the momentum term to the left hand side, and then factor the resulting expression as a difference of squares:

$$\left(i\hbar \frac{\partial}{\partial t} + c\boldsymbol{\sigma}\cdot\mathbf{P}\right)\left(i\hbar \frac{\partial}{\partial t} - c\boldsymbol{\sigma}\cdot\mathbf{P}\right)\phi = m^2c^4\phi\,. \tag{16.5}$$

We now define the quantity $\tilde{\phi}$ by the relationship

$$\left(i\hbar \frac{\partial}{\partial t} - c\boldsymbol{\sigma}\cdot\mathbf{P}\right)\phi = -mc^2\tilde{\phi}\,. \tag{16.6}$$

Substituting this into (16.5), we see that

$$\left(i\hbar \frac{\partial}{\partial t} + c\boldsymbol{\sigma}\cdot\mathbf{P}\right)\tilde{\phi} = -mc^2\phi\,. \tag{16.7}$$

Equations (16.6) and (16.7) can be written together as a single matrix equation

$$\left[i\hbar \frac{\partial}{\partial t} - c\begin{pmatrix}\boldsymbol{\sigma}\cdot\mathbf{P} & 0\\ 0 & -\boldsymbol{\sigma}\cdot\mathbf{P}\end{pmatrix}\right]\begin{pmatrix}\phi\\ \tilde{\phi}\end{pmatrix} = \begin{pmatrix}0 & -mc^2\\ -mc^2 & 0\end{pmatrix}\begin{pmatrix}\phi\\ \tilde{\phi}\end{pmatrix}. \tag{16.8}$$

Now, up to this point, we have treated ϕ as our wave function, and $\tilde{\phi}$ as a half-way point defined by (16.6). Our result is the coupled first-order differential equations (16.8). Our goal is to find a first-order Schrödinger equation for our wave function. The key is to stop thinking of $\tilde{\phi}$ as being defined by (16.6), but rather to think of it as an independent piece of the wave function, so that the whole wave function is defined by ϕ and $\tilde{\phi}$ together, which we write as

$$\Psi \equiv \begin{pmatrix}\phi\\ \tilde{\phi}\end{pmatrix}.$$

Equation (16.8) will then become our Schrödinger equation, now first order in time,

$$i\hbar\frac{\partial}{\partial t}\Psi = c\boldsymbol{\alpha}\cdot\mathbf{P}\Psi + mc^2\beta\Psi\ , \tag{16.9}$$

where

$$\boldsymbol{\alpha} \equiv \begin{pmatrix} \boldsymbol{\sigma} & 0 \\ 0 & -\boldsymbol{\sigma} \end{pmatrix} \quad \text{and} \quad \beta \equiv \begin{pmatrix} 0 & -\mathbf{1} \\ -\mathbf{1} & 0 \end{pmatrix}.. \tag{16.10}$$

Equation (16.9) is the (free) Dirac equation, where $\boldsymbol{\alpha}$ and β are the Dirac matrices, 4×4 matrices defined by (16.10). The Hamiltonian is

$$H = c\boldsymbol{\alpha}\cdot\mathbf{P} + mc^2\beta\ .$$

It will prove useful to have handy the following identities for products of the Dirac matrices:

$$\alpha_i\alpha_j + \alpha_j\alpha_i = 2\delta_{ij},\quad \alpha_i\beta + \beta\alpha_i = 0,\quad \beta^2 = 1. \tag{16.11}$$

In other words, all four matrices have a square of one, and they all anti-commute with each other. They are also all Hermitian. There are other ways of writing them. Let U be any 4×4 unitary matrix, and define

$$\Psi' \equiv U\Psi,\quad \boldsymbol{\alpha}' \equiv U\boldsymbol{\alpha}U^\dagger,\quad \text{and}\quad \beta' \equiv U\beta U^\dagger\ .$$

Then by multiplying (16.9) on the left and inserting factors of $1 = U^\dagger U$ appropriately, it is easy to show it is equivalent to

$$i\hbar\frac{\partial}{\partial t}\Psi' = c\boldsymbol{\alpha}'\cdot\mathbf{P}\Psi' + mc^2\beta'\Psi'\ .$$

This is just obviously the Dirac equation, but with $\boldsymbol{\alpha}$ and β redefined. The new matrices $\boldsymbol{\alpha}'$ and β' will still be Hermitian and still satisfy the relations (16.11). In particular, for

$$U = \frac{1}{\sqrt{2}}\begin{pmatrix} \mathbf{1} & -\mathbf{1} \\ \mathbf{1} & \mathbf{1} \end{pmatrix},$$

the Dirac matrices will take the form

$$\boldsymbol{\alpha}' = \begin{pmatrix} 0 & \boldsymbol{\sigma} \\ \boldsymbol{\sigma} & 0 \end{pmatrix} \quad \text{and} \quad \beta' = \begin{pmatrix} \mathbf{1} & 0 \\ 0 & -\mathbf{1} \end{pmatrix}. \tag{16.12}$$

The version (16.12) (the *Dirac* representation) is preferred by those who do non-relativistic physics, and (16.10) (the *Chiral* representation) is better for ultrarelativistic particles, when the mass becomes negligible. We will stick with the Chiral representation because it is slightly simpler for our purposes.

B. Solving the Free Dirac Equation

We would like to solve the time-independent Dirac equation, which is simply

$$\left(c\boldsymbol{\alpha}\cdot\mathbf{P}+mc^2\beta\right)\psi=E\psi\,.$$

We expect to find plane wave solutions of the form $\psi=u(\mathbf{k})e^{i\mathbf{k}\cdot\mathbf{r}}$, where u is independent of $\mathbf{r}$. Substituting this expression in, we find

$$\left(c\boldsymbol{\alpha}\cdot\mathbf{P}+mc^2\beta\right)u(\mathbf{k})e^{i\mathbf{k}\cdot\mathbf{r}}=\begin{pmatrix}c\hbar\boldsymbol{\sigma}\cdot\mathbf{k} & -mc^2\\ -mc^2 & -c\hbar\boldsymbol{\sigma}\cdot\mathbf{k}\end{pmatrix}u(\mathbf{k})e^{i\mathbf{k}\cdot\mathbf{r}}=Eu(\mathbf{k})e^{i\mathbf{k}\cdot\mathbf{r}}\,. \quad (16.13)$$

We are thus trying to solve this eigenvalue equation. As a first step, we consider the 2×2 matrix $\boldsymbol{\sigma}\cdot\mathbf{k}$, which when squared yields $(\boldsymbol{\sigma}\cdot\mathbf{k})^2=\mathbf{k}^2=k^2$, and therefore has eigenvalues $\pm k$. Let us define the two eigenstates of this matrix $\phi_\pm$, so that $(\boldsymbol{\sigma}\cdot\mathbf{k})\phi_\pm=\pm k\phi_\pm$. In explicit form, if you need them, one can show that if $\mathbf{k}$ is in the spherical direction denoted by θ and ϕ, we have

$$\phi_+=\begin{pmatrix}\cos\left(\frac{1}{2}\theta\right)\\ \sin\left(\frac{1}{2}\theta\right)e^{i\phi}\end{pmatrix}\quad\text{and}\quad\phi_-=\begin{pmatrix}-\sin\left(\frac{1}{2}\theta\right)\\ \cos\left(\frac{1}{2}\theta\right)e^{i\phi}\end{pmatrix}.$$

Then we will guess that we can find solutions of (16.13) of the form

$$u(\mathbf{k})=\begin{pmatrix}a\phi_\pm\\ b\phi_\pm\end{pmatrix}. \quad (16.14)$$

Substituting this into (16.13), we find

$$E\begin{pmatrix}a\phi_\pm\\ b\phi_\pm\end{pmatrix}=\begin{pmatrix}c\hbar\boldsymbol{\sigma}\cdot\mathbf{k} & -mc^2\\ -mc^2 & -c\hbar\boldsymbol{\sigma}\cdot\mathbf{k}\end{pmatrix}\begin{pmatrix}a\phi_\pm\\ b\phi_\pm\end{pmatrix}=\begin{pmatrix}\left(-bmc^2\pm ac\hbar k\right)\phi_\pm\\ \left(-amc^2\mp bc\hbar k\right)\phi_\pm\end{pmatrix}.$$

This yields the two equations

$$-\frac{a}{b}=\frac{E\pm c\hbar k}{mc^2}=\frac{mc^2}{E\mp c\hbar k}\,. \quad (16.15)$$

Cross-multiplying leads to the equation $E^2-c^2\hbar^2k^2=m^2c^4$, exactly what we want. Up to normalization, we can solve (16.15) for a and b, and then substitute into (16.14), yielding two solutions for each value of $\mathbf{k}$: [1]

$$\psi_\pm^u(\mathbf{r})=u_\pm(\mathbf{k})e^{i\mathbf{k}\cdot\mathbf{r}}=\begin{pmatrix}\sqrt{E\pm c\hbar k}\,\phi_\pm\\ -\sqrt{E\mp c\hbar k}\,\phi_\pm\end{pmatrix}e^{i\mathbf{k}\cdot\mathbf{r}}\,, \quad (16.16)$$

[1] If you wish to use wave functions of amplitude 1, these should be divided by $\sqrt{2E}$. For technical reasons this proves to be inconvenient, though it is irrelevant for us.

where $E = \sqrt{c^2\hbar^2k^2 + m^2c^4}$.

What are these two solutions? Obviously, they have the same momentum $\mathbf{p} = \hbar\mathbf{k}$. It turns out that the spin operator in the Dirac equation is given by

$$\mathbf{S} = \tfrac{1}{2}\hbar\mathbf{\Sigma}, \quad \text{where} \quad \mathbf{\Sigma} = \begin{pmatrix} \boldsymbol{\sigma} & 0 \\ 0 & \boldsymbol{\sigma} \end{pmatrix}. \tag{16.17}$$

If we measure the spin along the direction the particle is traveling we will find

$$\left(\hat{\mathbf{k}} \cdot \mathbf{S}\right)\psi_\pm = \tfrac{1}{2}\hbar \begin{pmatrix} \hat{\mathbf{k}} \cdot \boldsymbol{\sigma} & 0 \\ 0 & \hat{\mathbf{k}} \cdot \boldsymbol{\sigma} \end{pmatrix} \psi_\pm = \pm\tfrac{1}{2}\hbar\psi_\pm .$$

Thus it is in an eigenstate of spin in this direction. Of course, linear combinations of the two solutions (16.16) are also allowed. Hence the Dirac equation predicts two positive energy solutions for every value of the wave number **k** corresponding to the two spin states.

The eigenvalue equation (16.14) involves a 4×4 matrix, and hence should have four eigenvectors, not two. This suggests that we have somehow missed two solutions. Indeed, we have, and the problem is they have negative energy. They work out to be

$$\psi_\pm^v(\mathbf{r}) = v_\pm(\mathbf{k})e^{-i\mathbf{k}\cdot\mathbf{r}} = \begin{pmatrix} \sqrt{-E \mp c\hbar k}\,\phi_\mp \\ \sqrt{-E \pm c\hbar k}\,\phi_\mp \end{pmatrix} e^{-i\mathbf{k}\cdot\mathbf{r}} ,$$

where $E = -\sqrt{c^2\hbar^2k^2 + m^2c^4}$, as can be verified by direct substitution into the time-independent Dirac equation. It has momentum $-\hbar\mathbf{k}$ and spin along the direction $\hat{\mathbf{k}}$ of $\mp\tfrac{1}{2}\hbar$ (which makes it look like we mislabeled these solutions). But what do these solutions mean?

Dirac came up with the following solution. Dirac reasoned that because these states had negative energy, the ground state would be a state where these particles were present, not for just one momentum **p**, but for all momenta. He reasoned that since electrons were fermions, they satisfied the Pauli exclusion principle. Hence once you "filled" these states, there was no lower energy state. He suggested that what we normally term the "vacuum" is not truly empty, but rather is filled with electrons sitting in all the negative energy states. We cannot notice this "sea" of states because it is just the normal state of affairs.

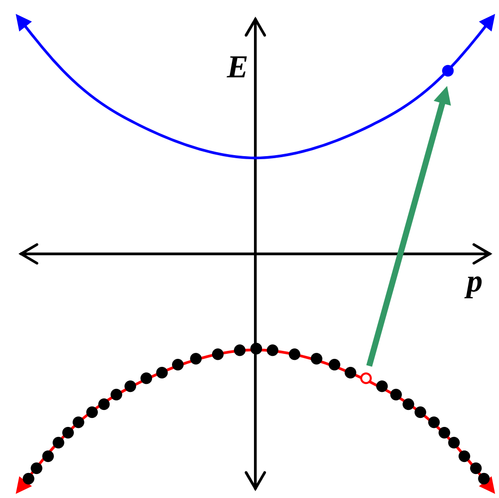


Figure 16-1: The Dirac equation has both positive (blue curve) and negative (red) energy solutions. Dirac assumed all the negative energy states were "filled" with an undetectable sea of electrons (black dots). Sufficient energy can move (green arrow) one of these electrons from a negative energy state to a positive energy state, producing a visible hole (open red circle) and an electron (blue dot).

Does this mean these negative energy states are irrelevant? Not at all. Suppose we applied a perturbation, say an electromagnetic pulse, of sufficient energy to take one of these negative energy states and promote it to a positive energy state. We would instantly "see" an electron that had not been there previously, as illustrated in Fig. 16-1. We would also simultaneously "see" a missing state from the negative energy sea, much as a bubble underwater indicates an absence of water. This "hole," as he called it, would be perceived as an absence of momentum $-\hbar\mathbf{k}$, (or in other words, a momentum $\hbar\mathbf{k}$), an absence of spin angular momentum $\mp\frac{1}{2}\hbar$ in the direction of $\hat{\mathbf{k}}$ (spin $\pm\frac{1}{2}\hbar$), an absence of energy $-\sqrt{c^2\hbar^2k^2+m^2c^4}$ (or a presence of enerby $E=\sqrt{c^2\hbar^2k^2+m^2c^4}$) and an absence of charge – e (or $q=+e$). In other words, we would see a particle identical to the electron, with the same mass and spin, except having the opposite charge. Dirac assumed this particle was the proton (and was puzzled why it didn't have the same mass), but we now recognize it as a separate particle, the positron, also known as the anti-electron. Dirac's arguments can be generalized to other spin-1/2 particle, and, in fact, we now expect every elementary particle to have an anti-particle, and, indeed, all particles do apparently have anti-particles (though some particles, like the photon, are their own anti-particle).

C. Electromagnetic Interactions and the Hydrogen Atom

We now wish to include electromagnetic interactions in our Hamiltonian. This is an easy matter: we simply change $\mathbf{P}$ to $\boldsymbol{\pi}=\mathbf{P}+e\mathbf{A}$ and then add the electrostatic potential energy $-eU$ to yield

$$H=c\boldsymbol{\alpha}\cdot\left[\mathbf{P}+e\mathbf{A}\left(\mathbf{R},t\right)\right]-eU\left(\mathbf{R},t\right)+mc^2\beta\,.$$

Let's try solving a particularly difficult and interesting problem in this case, namely, hydrogen, with potential $U=k_e e\big/\left|\mathbf{R}\right|$. Then our Hamiltonian is

$$H=c\boldsymbol{\alpha}\cdot\mathbf{P}-\frac{k_e e^2}{\left|\mathbf{R}\right|}+mc^2\beta=c\boldsymbol{\alpha}\cdot\mathbf{P}-\frac{\alpha\hbar c}{\left|\mathbf{R}\right|}+mc^2\beta\,,$$

where we have used the fine structure constant $\alpha=k_e e^2\big/\hbar c$ (not to be confused with $\boldsymbol{\alpha}$) to rewrite the potential term. We will be trying to find eigenstates of this equation, solutions of the time-independent Schrödinger equation

$$E\psi=\left(c\boldsymbol{\alpha}\cdot\mathbf{P}-\frac{\alpha\hbar c}{r}+mc^2\beta\right)\psi\,,$$

$$\left(E+\frac{\alpha\hbar c}{r}\right)\psi=\left(c\boldsymbol{\alpha}\cdot\mathbf{P}+mc^2\beta\right)\psi\,.$$

We now let the operator on the right act a second time on both sides to yield

$$\left(c\boldsymbol{\alpha}\cdot\mathbf{P}+mc^2\beta\right)\left(E+\frac{\alpha\hbar c}{r}\right)\psi=\left(c\boldsymbol{\alpha}\cdot\mathbf{P}+mc^2\beta\right)^2\psi\,.$$

On the right hand side, we can use the fact that all four matrices $\boldsymbol{\alpha}$ and β anti-commute with each other, so the cross terms all vanish, and their squares are all the identity matrix. On the left side, we note that if the factor of $\left(c\boldsymbol{\alpha}\cdot\mathbf{P}+mc^2\beta\right)$ were allowed to act on the wave function, we would only get another factor of $\left(E+\alpha\hbar c/r\right)$. However, the derivative $\mathbf{P}$ can also act on the potential $\alpha\hbar c/r$, yielding another term. The result is

$$\left(E+\frac{\alpha\hbar c}{r}\right)^2\psi+\frac{i\alpha\hbar^2c^2}{r^2}\left(\boldsymbol{\alpha}\cdot\hat{\mathbf{r}}\right)\psi=\left(c^2\mathbf{P}^2+m^2c^4\right)\psi\,.$$

We now notice something interesting: The only matrix in this whole equation is $\boldsymbol{\alpha}$, which is block-diagonal. Therefore, if we write our wave function ψ in terms of two pairs of components, as we originally defined it, we would find that the equations for ϕ and $\tilde{\phi}$ completely decouple.[1] Hence we can focus on one at a time. It is not hard to show that the two yield identical equations, so we will focus exclusively on ϕ, for which our equation is

$$\left\{E^2+\frac{2\alpha\hbar cE}{r}+\frac{\hbar^2c^2}{r^2}\left[\alpha^2+i\alpha\left(\boldsymbol{\sigma}\cdot\hat{\mathbf{r}}\right)\right]\right\}\phi=\left(c^2\mathbf{P}^2+m^2c^4\right)\phi\,. \qquad (16.18)$$

Our problem is spherically symmetric, so we should probably switch to spherical coordinates. With the help of (A.22d) and (7.23), it is not hard to show that in spherical coordinates,

$$\mathbf{P}^2\phi=-\frac{\hbar^2}{r}\frac{\partial^2}{\partial r^2}\left(r\phi\right)+\frac{\mathbf{L}^2}{r^2}\phi\,.$$

Substituting this into (16.18) and rearranging a bit, we have

$$\left(E^2-m^2c^4\right)\phi=-\frac{\hbar^2c^2}{r}\frac{\partial^2}{\partial r^2}\left(r\phi\right)-\frac{2\alpha\hbar cE}{r}\phi+\frac{\hbar^2c^2}{r^2}\left(\frac{\mathbf{L}^2}{\hbar^2}-\alpha^2-i\alpha^2\boldsymbol{\sigma}\cdot\hat{\mathbf{r}}\right)\phi\,. \qquad (16.19)$$

We note that all the angular and spin-dependence of this expression is contained in the last factor, which we define as A, so that

$$A\equiv\frac{\mathbf{L}^2}{\hbar^2}-\alpha^2-i\alpha\boldsymbol{\sigma}\cdot\hat{\mathbf{r}}\,.$$

It makes sense to try to factor ϕ into an angular and radial part, just like we did for non-relativistic Hydrogen. We let

$$\phi\left(\mathbf{r}\right)=R\left(r\right)\Upsilon\left(\theta,\phi\right),$$

where $R\left(r\right)$ is an ordinary function, but $\Upsilon\left(\theta,\phi\right)$ has two components, so it has both the angular and spin dependence. Substituting this form into (16.19), we have

[1] This is why we chose the chiral representation, the decoupling is far less obvious in the Dirac representation.

$$\left(E^2 - m^2c^4\right)R(r)\Upsilon(\theta,\phi) = -\frac{\hbar^2c^2}{r}\frac{\partial^2}{\partial r^2}\left[rR(r)\right]\Upsilon(\theta,\phi) - \frac{2\alpha\hbar cE}{r}R(r)\Upsilon(\theta,\phi)$$
$$+\frac{\hbar^2c^2}{r^2}R(r)A\Upsilon(\theta,\phi).$$

We'd like our angular functions $\Upsilon(\theta,\phi)$ to be eigenstates of *A*. This is the equivalent of finding the spherical harmonics, with the added complication of spin, though our primary interest here is only finding the eigenvalues of *A*.

To find the eigenvalues of *A*, consider first that the original Hamiltonian must be rotationally invariant, and hence commutes with all components of **J**, and specifically with $\mathbf{J}^2$ and J_z. It therefore makes sense to try to work with eigenstates of these two operators. We already know that the angular and spin states of a spherically symmetric problem can be written in the basis $\left|l, j, m_j\right\rangle$ (we have suppressed the spin label $s = \frac{1}{2}$) . Since $\mathbf{J}^2$ and J_z commute with the Hamiltonian, it is hardly surprising that they commute with *A*, and therefore *A* can only connect states with the same values of *j* and m_j. Thus the only non-zero matrix elements of *A* in this basis are

$$\left\langle l, j, m_j \middle| A \middle| l', j, m_j \right\rangle = \left\langle l, j, m_j \middle| \left(\frac{\mathbf{L}^2}{\hbar^2} - \alpha^2 - i\alpha\boldsymbol{\sigma}\cdot\hat{\mathbf{r}}\right) \middle| l', j, m_j \right\rangle. \tag{16.21}$$

Since $j = l \pm \frac{1}{2}$, there are only two possible values for *l*, and hence finding the eigenstates and eigenvalues of *A* is reduced to the problem of diagonalizing a 2×2 matrix.

The first two terms in (16.21) are obviously diagonal in this basis, so we see that

$$\left\langle l, j, m_j \middle| \left(\mathbf{L}^2/\hbar^2 - \alpha^2\right) \middle| l', j, m_j \right\rangle = \delta_{ll'}\left(l^2 + l - \alpha^2\right).$$

The last term is more problematic. If you rewrite $\boldsymbol{\sigma}\cdot\hat{\mathbf{r}} = \boldsymbol{\sigma}\cdot\mathbf{r}/r$, and then recall that the operator R (which becomes **r**) connects only states which differ by one value of *l*, you will realize that the *on*-diagonal components of this term must vanish, so

$$\left\langle l, j, m_j \middle| \boldsymbol{\sigma}\cdot\hat{\mathbf{r}} \middle| l, j, m_j \right\rangle = 0.$$

On the other hand, we know that $\left(\boldsymbol{\sigma}\cdot\hat{\mathbf{r}}\right)^2 = \mathbf{1}$, the identity matrix. It follows that

$$1 = \left\langle l, j, m_j \middle| \left(\boldsymbol{\sigma}\cdot\hat{\mathbf{r}}\right)\left(\boldsymbol{\sigma}\cdot\hat{\mathbf{r}}\right) \middle| l, j, m_j \right\rangle = \sum_{l'=j\pm\frac{1}{2}} \left\langle l, j, m_j \middle| \boldsymbol{\sigma}\cdot\hat{\mathbf{r}} \middle| l', j, m_j \right\rangle \left\langle l', j, m_j \middle| \boldsymbol{\sigma}\cdot\hat{\mathbf{r}} \middle| l, j, m_j \right\rangle$$
$$= \sum_{l'=j\pm\frac{1}{2}} \left|\left\langle l, j, m_j \middle| \boldsymbol{\sigma}\cdot\hat{\mathbf{r}} \middle| l', j, m_j \right\rangle\right|^2,$$

where we have inserted a complete set of intermediate states. However, there are only two terms in the sum, and one of them is zero, so the other one must be a number of magnitude one.[1] In other words,

$$\left\langle j-\tfrac{1}{2}, j, m_j \middle| \boldsymbol{\sigma}\cdot\hat{\mathbf{r}} \middle| j+\tfrac{1}{2}, j, m_j \right\rangle = \left\langle j+\tfrac{1}{2}, j, m_j \middle| \boldsymbol{\sigma}\cdot\hat{\mathbf{r}} \middle| j-\tfrac{1}{2}, j, m_j \right\rangle^* = \eta, \quad \text{where} \quad |\eta|^2 = 1 .$$

[1] Actually, it is one, but we won't need this fact.

We now know every matrix element of A; in the basis where we put $l = j - \frac{1}{2}$ first and $l = j + \frac{1}{2}$ second, A takes the form

$$A = \begin{pmatrix} \left(j-\frac{1}{2}\right)\left(j+\frac{1}{2}\right)-\alpha^2 & -i\alpha\eta \\ -i\alpha\eta^* & \left(j+\frac{1}{2}\right)\left(j+\frac{3}{2}\right)-\alpha^2 \end{pmatrix}.$$

It is a straightforward matter to find the eigenvalues of this matrix, which turn out to be

$$\left(j+\tfrac{1}{2}\right)^2 - \alpha^2 \pm \sqrt{\left(j+\tfrac{1}{2}\right)^2 - \alpha^2}\,.$$

It is very helpful to define the quantity

$$\lambda_j \equiv \sqrt{\left(j+\tfrac{1}{2}\right)^2 - \alpha^2}\,. \tag{16.22}$$

Then our eigenvalues are $\lambda_j^2 \pm \lambda_j$. Hence for every value of j and m_j we find two solutions $\Upsilon_{j,\pm}^{m_j}(\theta,\phi)$ satisfying

$$A\Upsilon_{j,\pm}^{m_j}(\theta,\phi) = \left(\frac{\mathbf{L}^2}{\hbar^2} - \alpha^2 - i\alpha\boldsymbol{\sigma}\cdot\hat{\mathbf{r}}\right)\Upsilon_{j,\pm}^{m_j}(\theta,\phi) = \left(\lambda_j^2 \pm \lambda_j\right)\Upsilon_{j,\pm}^{m_j}(\theta,\phi).$$

Substituting this into (16.19), we see that the angular portion cancels out, and we are left with two very similar radial equations,

$$\left(E^2 - m^2c^4\right)R(r) = -\frac{\hbar^2c^2}{r}\frac{d^2}{dr^2}\left[rR(r)\right] - \frac{2\alpha\hbar cE}{r}R(r) + \frac{\hbar^2c^2\left(\lambda_j^2 \pm \lambda_j\right)}{r^2}R(r).$$

Solving this will prove to be quick, because of its remarkable similarity to the standard hydrogen atom. To make the comparison as obvious as possible, first divide by $2E$.

$$\frac{E^2 - m^2c^4}{2E}R(r) = -\frac{\hbar^2c^2}{2Er}\frac{d^2}{dr^2}\left[rR(r)\right] - \frac{\alpha\hbar c}{r}R(r) + \frac{\hbar^2c^2}{2E}\frac{\lambda_j^2 \pm \lambda_j}{r^2}R(r). \tag{16.23}$$

Compare this to the radial equation for hydrogen, eq. (7.41), which we reproduce here, rewritten slightly:

$$ER(r) = -\frac{\hbar^2}{2\mu r}\frac{d^2}{dr^2}\left[rR(r)\right] - \frac{\alpha\hbar c}{r}R(r) + \frac{\hbar^2}{2\mu}\frac{l^2+l}{r^2}R(r). \tag{16.24}$$

Comparing (16.23) and (16.24), we see that the latter can be transformed into the former if we identify

$$E \to \frac{E^2 - m^2c^4}{2E}, \quad \mu \to \frac{E}{c^2}, \quad l^2 + l \to \lambda_j^2 \pm \lambda_j\,.$$

The last transformation must be treated as two separate cases, but it is pretty easy to see that the two cases are

$$l \to \lambda_j \quad \text{or} \quad l \to \lambda_j - 1.$$

The point is that we can now instantly use every equation we derived from hydrogen, we just need to make the corresponding transformations. For example, our formula for the radial wave function will take the form (similar to (7.50a))

$$R_{nl}\left(r\right)=e^{-r/a}\sum_{p=\lambda_J}^{\nu-1} f_p r^p \quad \text{or} \quad R_{nl}\left(r\right)=e^{-r/a}\sum_{p=\lambda_J-1}^{\nu-1} f_p r^p , \tag{16.25}$$

where a is given by (similar to (7.42)):

$$\frac{E^2-m^2c^4}{2E}=-\frac{\hbar^2c^2}{2Ea^2}, \quad \text{or} \quad a=\frac{\hbar c}{\sqrt{m^2c^4-E^2}} .$$

Equations (16.25) require a bit of discussion. Note that the lower limit on the sum is *not* an integer, and therefore the powers p of r are non-integer as well. The upper limit ν will therefore *also* not be an integer, but it will differ from the lower limit by an integer; that is $\nu=\lambda_j+k$,where k is a positive integer in the first case, and a non-negative integer in the second case.

The energies are given by an equation analogous to (7.51)

$$\frac{E^2-m^2c^4}{2E}=-\frac{Ek_e^2e^4}{2\hbar^2c^2\nu^2}=-\frac{E\alpha^2}{2\left(\lambda_j+k\right)^2},$$

$$E=mc^2\left[1+\alpha^2\left(\lambda_j+k\right)^{-2}\right]^{-\frac{1}{2}} . \tag{16.26}$$

This, together with (16.22), gives us the energies. It should be noted that in (16.26), k can be zero or a positive integer. When it is zero, we only have one case, but when k is positive, we will have two distinct cases, corresponding to the two angular functions $\Upsilon_{j,\pm}^{m_j}\left(\theta,\phi\right)$.

If we are dealing with a hydrogen-like atom, rather than true hydrogen, the only change is to substitute $\alpha\to Z\alpha$. So the more general version of (16.22) and (16.26) is

$$\lambda_j=\sqrt{\left(j+\tfrac{1}{2}\right)^2-Z^2\alpha^2} , \tag{16.27a}$$

$$E=mc^2\left[1+Z^2\alpha^2\left(\lambda_j+k\right)^{-2}\right]^{-\frac{1}{2}} . \tag{16.27b}$$

It is helpful to expand these in powers of the fine structure constant to understand what the various choices correspond to. We find, to fourth order in α ,

$$E=mc^2-\frac{mc^2\alpha^2Z^2}{2\left(j+\frac{1}{2}+k\right)^2}+\frac{mc^2\alpha^4Z^4}{\left(j+\frac{1}{2}+k\right)^4}\left(\frac{3}{8}-\frac{j+\frac{1}{2}+k}{2j+1}\right)+\cdots .$$

Looking at these terms order by order, it is easy to identify them. The first term is the rest energy of an electron. The second is the leading order binding energy. Indeed, since j is half-integer, the combination $j+\frac{1}{2}+k$ is an integer, which we name n, and the last term is simply the first relativistic correction. We therefore have

$$E = mc^2 - \frac{mc^2\alpha^2 Z^2}{2n^2} + \frac{mc^2\alpha^4 Z^4}{n^4}\left(\frac{3}{8} - \frac{n}{2j+1}\right) + \cdots, \tag{16.28}$$

with now the restriction that $n \geq j + \frac{1}{2}$. Indeed, the same restriction occurs for non-relativistic hydrogen. When $n > j + \frac{1}{2}$, there are two different possibilities with exactly the same energy (corresponding to $l = j \pm \frac{1}{2}$), while for $n = j + \frac{1}{2}$, there is only one (since $l = j + \frac{1}{2}$ is no longer allowed). The final expression in (16.28) is simply the first relativistic correction. The *j*-dependence is reflecting the conventional spin-orbit coupling, though other effects are included as well. Note, as expected, the corrections grow as powers of αZ, which means that larger *Z*'s will have much larger effects. In most practical situations, such atoms will in fact be neutral (or nearly neutral), and hence they won't be hydrogen-like at all.

It is interesting to note that the energy (16.27b) depends only on *j* and *k*, or in conventional notation, *j* and *n*. This means that, for example, the $2s_{1/2}$ and $2p_{1/2}$ levels are *still* exactly degenerate, if we ignore hyperfine interactions. This is surprising, because there is no evident symmetry protecting them. There *are* interactions that split this apparent degeneracy, but they come about by interactions with the quantized electromagnetic field, the subject of the next chapter.

Despite the successes of the Dirac equation, the awkward way it deals with anti-particles and other problems ultimately led to its abandonment as an approach to developing a fully relativistic theory of particles. Due to its complications, we will henceforth ignore it, and use non-relativistic electrons whenever possible. But electromagnetic waves, which always move at the speed of light, must be quantized in a fully relativistic formalism.

Problems for Chapter 16

1. For the free Dirac equation, define the probability density as $\rho = \psi^\dagger \psi$ and the probability current as $\mathbf{J} = c\psi^\dagger \boldsymbol{\alpha} \psi$. Show that probability is locally conserved, i.e., that $\partial\rho/\partial t + \nabla \cdot \mathbf{J} = 0$. Will this equation still be valid in the presence of electromagnetic effects coming from $\mathbf{A}(\mathbf{r},t)$ and $U(\mathbf{r},t)$?

2. In the class notes, we claimed that the spin was defined by $\mathbf{S} = \frac{1}{2}\hbar\boldsymbol{\Sigma}$, eq. (16.17). To make sure this is plausible:
   a) Demonstrate that **S** satisfies proper commutations relations $\left[S_i, S_j\right] = \sum_k i\hbar\varepsilon_{ijk} S_k$.
   b) Work out the six commutators $[\mathbf{L}, H]$ and $[\mathbf{S}, H]$ for the free Dirac Hamiltonian.
   c) Show that $[\mathbf{J}, H] = 0$, where $\mathbf{J} = \mathbf{L} + \mathbf{S}$.

XVII. Quantization of Electromagnetic Fields

When Max Planck first "discovered" quantum mechanics, it was by conjecturing that electromagnetic waves come in quantized packets of energy $E = \hbar\omega$. And yet here we are, 300 pages of notes later, and we have yet to quantize the electromagnetic field. This is because electromagnetism presents some special challenges. Fortunately, these challenges have been generally overcome, and we have a fully relativistic theory of the electromagnetic field. Ultimately, we will want to interact electromagnetic waves with electrons or other particles, but for now, let us try to quantize the pure EM field.

A. Gauge Choice and Energy

One complication that is especially annoying about electromagnetism is that it will turn out to be necessary to work with the vector and scalar potential, $\mathbf{A}(\mathbf{r},t)$ and $U(\mathbf{r},t)$, not the electric and magnetic fields **E** and **B** directly. As we discussed in chapter 9, we must make a gauge choice; that is, we have to decide which of several possible specific forms for **A** and *U* we will use to describe the electric and magnetic fields. A gauge transformation is given by (9.11), repeated here:

$$U'(\mathbf{r},t) = U(\mathbf{r},t) - \frac{\partial}{\partial t}\chi(\mathbf{r},t) \quad \text{and} \quad \mathbf{A}'(\mathbf{r},t) = \mathbf{A}(\mathbf{r},t) + \nabla\chi(\mathbf{r},t). \tag{17.1}$$

Though several different gauges are useful for different purposes, we will choose, in this case, to select the Coulomb gauge, defined by the constraint

$$\nabla \cdot \mathbf{A}(\mathbf{r},t) = 0.$$

Can such a gauge choice be made? The answer is yes. Suppose, for example, that this were not the case; that is, suppose $\nabla \cdot \mathbf{A} \neq 0$. Then define $\chi(\mathbf{r},t)$) to be the solution of the equation

$$\nabla^2 \chi(\mathbf{r},t) = -\nabla \cdot \mathbf{A}(\mathbf{r},t) \tag{17.2}$$

We know, in general, that such a solution always exists; indeed, it isn't hard to show that it is explicitly given by

$$\chi(\mathbf{r},t) = \int \frac{\nabla \cdot \mathbf{A}(\mathbf{r}',t)}{4\pi|\mathbf{r}-\mathbf{r}'|} d^3\mathbf{r}'.$$

Then it follows from (17.1) and (17.2) that $\nabla \cdot \mathbf{A}'(\mathbf{r},t) = 0$.

In terms of the vector and scalar potential, the electric and magnetic fields are given by (9.6) and (9.7), repeated here

$$\begin{aligned} \mathbf{E}(\mathbf{r},t) &= -\dot{\mathbf{A}}(\mathbf{r},t) - \nabla U(\mathbf{r},t), \\ \mathbf{B}(\mathbf{r},t) &= \nabla \times \mathbf{A}(\mathbf{r},t). \end{aligned} \tag{17.3}$$

The first of Maxwell's equations (Coulomb's Law) states that[1]

$$\rho(\mathbf{r},t)=\varepsilon_0\nabla\cdot\mathbf{E}(\mathbf{r},t)=-\varepsilon_0\nabla\cdot\left[\dot{\mathbf{A}}(\mathbf{r},t)+\nabla U(\mathbf{r},t)\right]=-\varepsilon_0\nabla^2U(\mathbf{r},t).$$

Note there are no time derivatives in this equation, so the scalar potential is determined, in this gauge, by the instantaneous charge density

$$U(\mathbf{r},t)=\int\frac{\rho(\mathbf{r}',t)}{4\pi\varepsilon_0\left|\mathbf{r}-\mathbf{r}'\right|}d^3\mathbf{r}',$$

the same formula we have been using all along. All of the dynamics, and interesting quantum mechanical effects, will come from the vector potential **A**. In the absence of charges, the scalar potential will be trivial, $U(\mathbf{r},t)=0$.

We now want to write the classical Hamiltonian, which is just the energy formula. The energy density of the electromagnetic fields is[2]

$$u(\mathbf{r},t)=\tfrac{1}{2}\varepsilon_0\mathbf{E}^2(\mathbf{r},t)+\tfrac{1}{2}\mu_0^{-1}\mathbf{B}^2(\mathbf{r},t)=\tfrac{1}{2}\varepsilon_0\left[\mathbf{E}^2(\mathbf{r},t)+c^2\mathbf{B}^2(\mathbf{r},t)\right]. \qquad (17.4)$$

so the energy of the fields is given by

$$E=\tfrac{1}{2}\varepsilon_0\int\left[\mathbf{E}^2(\mathbf{r},t)+c^2\mathbf{B}^2(\mathbf{r},t)\right]d^3\mathbf{r}=\tfrac{1}{2}\varepsilon_0\int\left\{\dot{\mathbf{A}}^2(\mathbf{r},t)+c^2\left[\nabla\times\mathbf{A}(\mathbf{r},t)\right]^2\right\}d^3\mathbf{r}. \qquad (17.5)$$

Though it is not obvious, (17.5) is nothing more than a formula for an infinite number of coupled harmonic oscillators. Think of $\mathbf{A}(\mathbf{r},t)$ as an infinite number of independently varying "positions"; then the time derivative term is just like a kinetic energy term for a particle. The curl term is a derivative, which we can think about as the difference between $\mathbf{A}(\mathbf{r},t)$ at "adjacent" points, and hence this term is a coupling term.

B. Fourier Modes and Polarization Vectors

To make our work easier, we proceed to work in finite volume. We will imagine that the universe has volume $V=L^3$, possessing periodic boundary conditions in all three directions. Therefore, any function $\psi(\mathbf{r})$ will have the property

$$\psi(x+L,y,z)=\psi(x,y+L,z)=\psi(x,y,z+L)=\psi(x,y,z).$$

Any such function can written as a sum of Fourier modes,

$$\mathbf{A}(\mathbf{r},t)=\sum_{\mathbf{k}}\mathbf{A}_{\mathbf{k}}(t)e^{i\mathbf{k}\cdot\mathbf{r}}. \qquad (17.6)$$

[1] In previous chapters, we have avoided using ε_0, and preferred Coulomb's constant k_e. The two are related by $4\pi k_e\varepsilon_0=1$.

[2] See, for example, Jackson, *Classical Electrodynamics*, third edition (Wiley, 1999) equations (4.89), p. 166 and (5.148), p. 213

Because of the periodic boundary conditions, our **k**-values in the sum are not continuous, but discrete, so that

$$\mathbf{k} = \frac{2\pi}{L}\mathbf{n} = \frac{2\pi}{L}\left(n_x, n_y, n_z\right).$$

where **n** is a triplet of integers. The mode functions $\mathbf{A}_\mathbf{k}\left(t\right)$ are further restricted by the demand that they must lead to a real vector potential $\mathbf{A}\left(\mathbf{r},t\right)$, which requires that $\mathbf{A}_{-\mathbf{k}}\left(t\right) = \mathbf{A}_\mathbf{k}^*\left(t\right)$. Also, because we are working in Coulomb gauge, we must have $\nabla\cdot\mathbf{A} = 0$, which implies $\mathbf{k}\cdot\mathbf{A}_\mathbf{k}\left(t\right) = 0$.

Substituting (17.6) into (17.5), we see that the energy takes the form

$$E = \tfrac{1}{2}\varepsilon_0 \int \left\{ \left[\sum_\mathbf{k} \dot{\mathbf{A}}_\mathbf{k}\left(t\right) e^{i\mathbf{k}\cdot\mathbf{r}}\right]^2 + c^2\left[\sum_\mathbf{k} i\mathbf{k}\times\mathbf{A}_\mathbf{k}\left(t\right)e^{i\mathbf{k}\cdot\mathbf{r}}\right]^2 \right\} d^3\mathbf{r}$$

$$= \tfrac{1}{2}\varepsilon_0 \sum_\mathbf{k}\sum_{\mathbf{k}'}\int\left\{\dot{\mathbf{A}}_\mathbf{k}\left(t\right)\cdot\dot{\mathbf{A}}_{\mathbf{k}'}\left(t\right) + i^2c^2\left[\mathbf{k}\times\mathbf{A}_\mathbf{k}\left(t\right)\right]\cdot\left[\mathbf{k}'\times\mathbf{A}_{\mathbf{k}'}\left(t\right)\right]\right\} e^{i\mathbf{k}\cdot\mathbf{r}+i\mathbf{k}'\cdot\mathbf{r}} d^3\mathbf{r}.$$

The space integral is easy to do, $\int e^{i\mathbf{k}\cdot\mathbf{r}+i\mathbf{k}'\cdot\mathbf{r}} d^3\mathbf{r} = V\delta_{\mathbf{k},-\mathbf{k}'}$, which yields

$$E = \tfrac{1}{2}\varepsilon_0 V \sum_\mathbf{k}\left\{\dot{\mathbf{A}}_\mathbf{k}\left(t\right)\cdot\dot{\mathbf{A}}_{-\mathbf{k}}\left(t\right) + c^2\mathbf{k}^2\mathbf{A}_\mathbf{k}\left(t\right)\cdot\mathbf{A}_{-\mathbf{k}}\left(t\right)\right\}, \tag{17.7}$$

where we have used $\mathbf{k}\cdot\mathbf{A}_\mathbf{k}\left(t\right) = 0$ to simplify the dotted cross products. We now need to take advantage of the restriction $\mathbf{A}_{-\mathbf{k}}\left(t\right) = \mathbf{A}_\mathbf{k}^*\left(t\right)$. This allows us to simplify the terms in (17.7). It is also apparent that the sums in (17.7) contains pairs of identical terms. To avoid confusion later, we will divide the **k** values in half, treating half of them as positive; for example, we can define **k** > 0 as those values for which the first non-zero component of **k** is positive.[1] Then (17.7) becomes

$$E = \varepsilon_0 V \sum_{\mathbf{k}>0}\left\{\dot{\mathbf{A}}_\mathbf{k}\left(t\right)\cdot\dot{\mathbf{A}}_\mathbf{k}^*\left(t\right) + c^2\mathbf{k}^2\mathbf{A}_\mathbf{k}\left(t\right)\cdot\mathbf{A}_\mathbf{k}^*\left(t\right)\right\}. \tag{17.8}$$

We have successfully decoupled the different Fourier modes, but we still have vector quantities to deal with. Because of the restriction $\mathbf{k}\cdot\mathbf{A}_\mathbf{k}\left(t\right) = 0$, $\mathbf{A}_\mathbf{k}\left(t\right)$ has only two independent components. We define two orthonormal polarization vectors $\boldsymbol{\varepsilon}_{\mathbf{k}\sigma}$ where $\sigma = 1, 2$, chosen so that

$$\mathbf{k}\cdot\boldsymbol{\varepsilon}_{\mathbf{k}\sigma} = 0 \quad\text{and}\quad \boldsymbol{\varepsilon}_{\mathbf{k}\sigma}^*\cdot\boldsymbol{\varepsilon}_{\mathbf{k}\tau} = \delta_{\sigma\tau}.$$

We then write our modes $\mathbf{A}_\mathbf{k}\left(t\right)$ as

$$\mathbf{A}_\mathbf{k}\left(t\right) = \sum_{\sigma=1,2} A_{\mathbf{k}\sigma}\left(t\right)\boldsymbol{\varepsilon}_{\mathbf{k}\sigma}. \tag{17.9}$$

[1] This might leave you concerned about the special case **k** = 0; however, it is easily demonstrated that a gauge change can always eliminate such a space-independent mode.

Substituting this into (17.8), we have

$$E = \varepsilon_0 V \sum_{\mathbf{k}>0} \sum_{\sigma} \left[\dot{A}_{\mathbf{k}\sigma}(t) \cdot \dot{A}^*_{\mathbf{k}\sigma}(t) + c^2 \mathbf{k}^2 A_{\mathbf{k}\sigma}(t) A^*_{\mathbf{k}\sigma}(t) \right]. \tag{17.10}$$

We are now prepared to quantize our theory.

C. Quantizing the Electromagnetic Fields

Equation (17.10) is nothing more than a sum of complex harmonic oscillators. We therefore can take advantage of all of the work of section 5F and quickly quantize the theory. The classical theory we quantized in section 5F had an energy given by (5.25), $E = m\left(\dot{z}\dot{z}^* + \omega^2 z z^*\right)$. Comparison with (17.10) tells us that we can take over all our old formulas if we make the following associations:

$$m \to \varepsilon_0 V, \quad \omega \to \omega_k \equiv ck, \quad z \to A_{\mathbf{k}\sigma}.$$

We then simply copy equations like (5.29), without doing any additional work:

$$H = \sum_{\mathbf{k}>0} \sum_{\sigma} \hbar\omega_k \left(a^\dagger_{+,\mathbf{k},\sigma} a_{+,\mathbf{k},\sigma} + a^\dagger_{-,\mathbf{k},\sigma} a_{-,\mathbf{k},\sigma} + 1 \right).$$

Our notation is getting a bit unwieldy. At the moment, there are three indices on a, one denoting which of the two annihilation operators we are talking about for our complex variables $A_{k\sigma}$, one denoting the vector **k** (which is restricted to be positive), and one denoting the polarization. We can combine the first two into a single index **k** which is no longer restricted to be positive by defining $a_{+,\mathbf{k},\sigma} = a_{\mathbf{k},\sigma}$ and $a_{-,\mathbf{k},\sigma} = a_{-\mathbf{k},\sigma}$. The commutation relations for these operators is

$$\left[a_{\mathbf{k},\sigma}, a^\dagger_{\mathbf{k}',\sigma'} \right] = \delta_{\mathbf{k}\mathbf{k}'} \delta_{\sigma\sigma'}, \quad \left[a_{\mathbf{k},\sigma}, a_{\mathbf{k}',\sigma'} \right] = \left[a^\dagger_{\mathbf{k},\sigma}, a^\dagger_{\mathbf{k}',\sigma'} \right] = 0. \tag{17.11}$$

Then, splitting the constant term in half, we can rewrite the Hamiltonian in the more compact form

$$H = \sum_{\mathbf{k},\sigma} \hbar\omega_k \left(a^\dagger_{\mathbf{k}\sigma} a_{\mathbf{k}\sigma} + \tfrac{1}{2} \right) \quad \text{where} \quad \omega_k \equiv ck. \tag{17.12}$$

Note we have abbreviated $a_{\mathbf{k},\sigma}$ as $a_{\mathbf{k}\sigma}$, dropping the comma. The sum is no longer restricted to positive **k**-values.

The analog of equations (5.30) can then be written in terms of creation and annihilation operators

$$A_{\mathbf{k}\sigma} \to \sqrt{\frac{\hbar}{2\varepsilon_0 V \omega_k}} \left(a_{\mathbf{k}\sigma} + a^\dagger_{-\mathbf{k},\sigma} \right), \quad \dot{A}_{\mathbf{k}\sigma} \to i \sqrt{\frac{\hbar\omega_k}{2\varepsilon_0 V}} \left(a^\dagger_{-\mathbf{k},\sigma} - a_{\mathbf{k}\sigma} \right).$$

This allows us to write our vector potential with the help of (17.6) and (17.9)

$$\mathbf{A}(\mathbf{r}) = \sum_{\mathbf{k},\sigma} \sqrt{\frac{\hbar}{2\varepsilon_0 V \omega_k}} \left(a_{\mathbf{k}\sigma} + a^\dagger_{-\mathbf{k},\sigma} \right) \boldsymbol{\varepsilon}_{\mathbf{k}\sigma} e^{i\mathbf{k}\cdot\mathbf{r}}.$$

Our analysis has not produced a manifestly Hermitian expression for $\mathbf{A}(\mathbf{r})$, which is surprising, since its classical analog is always real. The complication has to do with the way the sums were temporarily restricted to $\mathbf{k}>0$, with the restriction $\mathbf{A}_{-\mathbf{k}}(t)=\mathbf{A}_{\mathbf{k}}^{*}(t)$. The effect is that we are forced to choose our polarization vectors such that $\boldsymbol{\varepsilon}_{-\mathbf{k},\sigma}=\boldsymbol{\varepsilon}_{\mathbf{k}\sigma}^{*}$. With this restriction, it is more useful to rewrite the final term by taking $\mathbf{k}\to-\mathbf{k}$, yielding the manifestly Hermitian expression

$$\mathbf{A}(\mathbf{r})=\sum_{\mathbf{k},\sigma}\sqrt{\frac{\hbar}{2\varepsilon_0 V\omega_k}}\left(\boldsymbol{\varepsilon}_{\mathbf{k}\sigma}e^{i\mathbf{k}\cdot\mathbf{r}}a_{\mathbf{k}\sigma}+\boldsymbol{\varepsilon}_{\mathbf{k}\sigma}^{*}e^{-i\mathbf{k}\cdot\mathbf{r}}a_{\mathbf{k}\sigma}^{\dagger}\right). \tag{17.13}$$

We can then take the curl of this expression to get the magnetic field. Furthermore, we can find an expression for the electric field by using our expression for $\dot{A}_{\mathbf{k}\sigma}$ for the time derivatives. Skipping many steps, the results are

$$\mathbf{E}(\mathbf{r})=\sum_{\mathbf{k},\sigma}\sqrt{\frac{\hbar\omega_k}{2\varepsilon_0 V}}\,i\left(\boldsymbol{\varepsilon}_{\mathbf{k}\sigma}e^{i\mathbf{k}\cdot\mathbf{r}}a_{\mathbf{k}\sigma}-\boldsymbol{\varepsilon}_{\mathbf{k}\sigma}^{*}e^{-i\mathbf{k}\cdot\mathbf{r}}a_{\mathbf{k}\sigma}^{\dagger}\right), \tag{17.14a}$$

$$\mathbf{B}(\mathbf{r})=\sum_{\mathbf{k},\sigma}\sqrt{\frac{\hbar}{2\varepsilon_0 V\omega_k}}\,i\mathbf{k}\times\left(\boldsymbol{\varepsilon}_{\mathbf{k}\sigma}e^{i\mathbf{k}\cdot\mathbf{r}}a_{\mathbf{k}\sigma}-\boldsymbol{\varepsilon}_{\mathbf{k}\sigma}^{*}e^{-i\mathbf{k}\cdot\mathbf{r}}a_{\mathbf{k}\sigma}^{\dagger}\right). \tag{17.14b}$$

In most circumstances, we will work with real polarizations, in which case (17.13) and (17.14) can be simplified.

Note that the time dependences in (17.13) and (17.14) have been dropped. This is because **A**, **E**, and **B** are now all to be interpreted as operators, which act on some sort of state vector. In particular, $\mathbf{E}(\mathbf{r})$ and $\mathbf{B}(\mathbf{r})$ are quantities that can be measured experimentally, whose values will be uncertain, due to the spread in whatever wave function you might be interested in ($\mathbf{A}(\mathbf{r})$ is not measurable, since it is not gauge invariant), just as the position ***x*** of a particle gets replaced by an operator *X* when we quantize the harmonic oscillator. The quantum states $|\psi\rangle$ are, however, far more complicated, and therefore require some additional comment.

D. Eigenstates of the Electromagnetic Fields

We focus for the moment on the Hamiltonian, given by (17.12), which is clearly just a sum of harmonic oscillators. We start by guessing that the ground state will be the state $|0\rangle$, the state annihilated by all the lowering operators, so $a_{\mathbf{k}\sigma}|0\rangle=0$. This state has energy $E_0=\sum\frac{1}{2}\hbar\omega_k=\infty$, thanks to the infinite number of terms in the sum. One might hope that this might have something to do with the finite volume, and that in the limit $V\to\infty$ this infinity might be spread throughout all of space, thereby rendering a relatively innocuous finite energy density, but a more careful analysis will show that in this limit, the energy density is infinite. How can we deal with this infinite energy?

The answer is deceptively simple. As always, adding a constant to the Hamiltonian has no effect on the physics. We always measure differences in energy, not absolute energy values, and hence we can simply rewrite (17.12) as

$$H = \sum_{\mathbf{k},\sigma} \hbar\omega_k a_{\mathbf{k}\sigma}^\dagger a_{\mathbf{k}\sigma} \quad \text{where} \quad \omega_k = ck\,. \tag{17.15}$$

The ground state now has energy zero.

An arbitrary eigenstate of H could be listed by simply listing the eigenstates of all the number operators $N_{\mathbf{k}\sigma} = a_{\mathbf{k}\sigma}^\dagger a_{\mathbf{k}\sigma}$, but since we have an infinite number of such operators, such a listing would become unwieldy. We therefore list only those states which have non-zero values for these operators, so we denote our states as

$$\left| n_1, \mathbf{k}_1, \sigma_1; n_2, \mathbf{k}_2, \sigma_2; \ldots; n_M, \mathbf{k}_M, \sigma_M \right\rangle, \tag{17.16}$$

with energy

$$E = \hbar\left(n_1\omega_1 + n_2\omega_2 + \cdots + n_M\omega_M\right).$$

We will describe such a quantum state as having n_1 photons of momentum $\hbar\mathbf{k}_1$ and polarization σ_1, n_2 photons of momentum $\hbar\mathbf{k}_2$ and polarization σ_2, etc. These states can be built up from the ground state (vacuum) in the usual way, so that

$$\left| n_1, \mathbf{k}_1, \sigma_1; n_2, \mathbf{k}_2, \sigma_2; \ldots; n_M, \mathbf{k}_M, \sigma_M \right\rangle = \frac{1}{\sqrt{n_1!\,n_2!\cdots n_M!}}\left(a_{\mathbf{k}_1\sigma_1}^\dagger\right)^{n_1}\left(a_{\mathbf{k}_2\sigma_2}^\dagger\right)^{n_2}\cdots\left(a_{\mathbf{k}_M\sigma_M}^\dagger\right)^{n_M}\left|0\right\rangle.$$

The order of the triplets in (17.16) is irrelevant. Creation and annihilation operators act as usual on the states (17.16):

$$a_{\mathbf{k}\sigma}\left|n, \mathbf{k}, \sigma; \ldots\right\rangle = \sqrt{n}\left|n-1, \mathbf{k}, \sigma; \ldots\right\rangle,$$
$$a_{\mathbf{k}\sigma}^\dagger\left|n, \mathbf{k}, \sigma; \ldots\right\rangle = \sqrt{n+1}\left|n+1, \mathbf{k}, \sigma; \ldots\right\rangle.$$

We will sometimes abbreviate our states still further. For example, if we know we will not be discussing more than one photon at a time, we might write the state as $\left|\mathbf{k}\sigma\right\rangle$.

E. Momentum of photons

Classically, a photon of energy $E = \hbar\omega$ should have a momentum $p = E/c = \hbar k$. Will this work quantum mechanically as well? In electromagnetism, the momentum density of the electromagnetic field is given by[1] $\mathbf{g} = \varepsilon_0 \mathbf{E}\times\mathbf{B}$. We need to integrate this over our volume V, using our explicit form of the electric and magnetic fields (17.14a,b):

$$\mathbf{P}_{em} = \varepsilon_0 \int \mathbf{E}\times\mathbf{B}\, d^3\mathbf{r} = \frac{\hbar i^2}{2V}\sum_{\mathbf{k}\sigma}\sum_{\mathbf{k}'\sigma'}\sqrt{\frac{\omega_k}{\omega_{k'}}}\int\left\{\begin{array}{l}\left(e^{i\mathbf{k}\cdot\mathbf{r}}\boldsymbol{\varepsilon}_{\mathbf{k}\sigma}a_{\mathbf{k}\sigma} - e^{-i\mathbf{k}\cdot\mathbf{r}}\boldsymbol{\varepsilon}_{\mathbf{k}\sigma}^* a_{\mathbf{k}\sigma}^\dagger\right)\times \\ \left[\mathbf{k}'\times\left(e^{i\mathbf{k}'\cdot\mathbf{r}}\boldsymbol{\varepsilon}_{\mathbf{k}'\sigma'}a_{\mathbf{k}'\sigma'} - e^{-i\mathbf{k}'\cdot\mathbf{r}}\boldsymbol{\varepsilon}_{\mathbf{k}'\sigma'}^* a_{\mathbf{k}'\sigma'}^\dagger\right)\right]\end{array}\right\} d^3\mathbf{r},$$

[1] Jackson, *Classical Electrodynamics*, third edition (Wiley, 199) equation (6.123), p. 262.

$$\mathbf{P}_{em} = \frac{\hbar}{2}\sum_{\mathbf{k}\sigma}\sum_{\mathbf{k}'\sigma'}\sqrt{\frac{\omega_k}{\omega_{k'}}}\begin{bmatrix} -\delta_{\mathbf{k},-\mathbf{k}'}\boldsymbol{\varepsilon}_{\mathbf{k}\sigma}\times\left(\mathbf{k}'\times\boldsymbol{\varepsilon}_{\mathbf{k}'\sigma'}\right)a_{\mathbf{k}\sigma}a_{\mathbf{k}'\sigma'} + \delta_{\mathbf{k},\mathbf{k}'}\boldsymbol{\varepsilon}_{\mathbf{k}\sigma}\times\left(\mathbf{k}'\times\boldsymbol{\varepsilon}^*_{\mathbf{k}'\sigma'}\right)a_{\mathbf{k}\sigma}a^\dagger_{\mathbf{k}'\sigma'} \\ +\delta_{\mathbf{k},\mathbf{k}'}\boldsymbol{\varepsilon}^*_{\mathbf{k}\sigma}\times\left(\mathbf{k}'\times\boldsymbol{\varepsilon}_{\mathbf{k}'\sigma'}\right)a^\dagger_{\mathbf{k}\sigma}a_{\mathbf{k}'\sigma'} - \delta_{\mathbf{k},-\mathbf{k}'}\boldsymbol{\varepsilon}^*_{\mathbf{k}\sigma}\times\left(\mathbf{k}'\times\boldsymbol{\varepsilon}^*_{\mathbf{k}'\sigma'}\right)a^\dagger_{\mathbf{k}\sigma}a^\dagger_{\mathbf{k}'\sigma'} \end{bmatrix}$$

$$= \tfrac{1}{2}\hbar\sum_{\mathbf{k}\sigma}\sum_{\sigma'}\left[\boldsymbol{\varepsilon}_{\mathbf{k}\sigma}\times\left(\mathbf{k}\times\boldsymbol{\varepsilon}^*_{\mathbf{k}\sigma'}\right)\left(a_{\mathbf{k}\sigma}a_{-\mathbf{k},\sigma'} + a_{\mathbf{k}\sigma}a^\dagger_{\mathbf{k}\sigma'}\right) + \boldsymbol{\varepsilon}^*_{\mathbf{k}\sigma}\times\left(\mathbf{k}\times\boldsymbol{\varepsilon}_{\mathbf{k}\sigma'}\right)\left(a^\dagger_{\mathbf{k}\sigma}a_{\mathbf{k}\sigma'} + a^\dagger_{\mathbf{k}\sigma}a^\dagger_{-\mathbf{k},\sigma'}\right)\right]$$

$$= \tfrac{1}{2}\hbar\sum_{\mathbf{k}\sigma}\sum_{\sigma'}\mathbf{k}\delta_{\sigma\sigma'}\left(a_{\mathbf{k}\sigma}a_{-\mathbf{k},\sigma'} + a_{\mathbf{k}\sigma}a^\dagger_{\mathbf{k}\sigma'} + a^\dagger_{\mathbf{k}\sigma}a_{\mathbf{k}\sigma'} + a^\dagger_{\mathbf{k}\sigma}a^\dagger_{-\mathbf{k},\sigma'}\right)$$

$$= \tfrac{1}{2}\hbar\sum_{\mathbf{k}\sigma}\mathbf{k}\left(a_{\mathbf{k}\sigma}a_{-\mathbf{k},\sigma} + a_{\mathbf{k}\sigma}a^\dagger_{\mathbf{k}\sigma} + a^\dagger_{\mathbf{k}\sigma}a_{\mathbf{k}\sigma} + a^\dagger_{\mathbf{k}\sigma}a^\dagger_{-\mathbf{k},\sigma}\right).$$

For each of the first terms $\mathbf{k}a_{\mathbf{k}\sigma}a_{-\mathbf{k},\sigma}$, there will be another term $-\mathbf{k}a_{-\mathbf{k}\sigma}a_{\mathbf{k},\sigma}$ which exactly cancels it. The same applies to the last term. The middle two terms can be combined with the help of (17.11) to yield

$$\mathbf{P}_{em} = \tfrac{1}{2}\hbar\sum_{\mathbf{k}\sigma}\mathbf{k}\left(1 + 2a^\dagger_{\mathbf{k}\sigma}a_{\mathbf{k}\sigma}\right).$$

The term that is just a sum of **k** will now cancel between the positive and negative allowed values of **k**, and the remaining term simplifies to

$$\mathbf{P}_{em} = \sum_{\mathbf{k}\sigma}\hbar\mathbf{k}a^\dagger_{\mathbf{k}\sigma}a_{\mathbf{k}\sigma},$$

which we simply interpret as photons having momentum $\hbar\mathbf{k}$, as expected.

F. Taking the infinite volume limit

We will commonly want to take the limit where the volume of the universe is increased to infinity. Generally, our strategy will be to keep the volume finite as long as possible, and then apply the limit only when necessary. Two formulas make this easy.

Consider first the following integral, in both the finite and infinite volume limit.

$$\int d^3\mathbf{r}\, e^{i\mathbf{k}\cdot\mathbf{r} - i\mathbf{k}'\cdot\mathbf{r}} = \begin{cases} V\delta_{\mathbf{k},\mathbf{k}'} & \text{if } V < \infty, \\ (2\pi)^3\delta^3(\mathbf{k} - \mathbf{k}') & \text{if } V = \infty. \end{cases}$$

This leads to our first rule: We want the former expression to turn into the latter as V increases to infinity, or in other words,

$$\lim_{V\to\infty}\left(V\delta_{\mathbf{k},\mathbf{k}'}\right) = (2\pi)^3\delta^3(\mathbf{k} - \mathbf{k}'). \tag{17.17}$$

The other expression comes from considering carefully any sum over momentum states. Consider first a one-dimensional sum of k-values. In 1D, in the finite volume limit, k can only take on the discrete values $k = n\Delta k$ where n is an integer, and $\Delta k = 2\pi/L$. In the large size limit, this spacing becomes very small. Indeed, the one-dimensional integral $\int f(k)\,dk$ is defined more or less as

$$\int f(k)\,dk \equiv \lim_{\Delta k\to 0} \Delta k \sum_n f(n\Delta k) = \lim_{L\to\infty} \frac{2\pi}{L} \sum_k f(k).$$

In one dimension, therefore, we see that the appropriate limit can be written as

$$\lim_{L\to\infty}\left[\frac{1}{L}\sum_k f(k)\right] = \int \frac{dk}{2\pi} f(k).$$

In three dimensions, this generalizes to

$$\lim_{V\to\infty}\left[\frac{1}{V}\sum_{\mathbf{k}} f(\mathbf{k})\right] = \int \frac{d^3\mathbf{k}}{(2\pi)^3} f(\mathbf{k}). \tag{17.18}$$

Indeed, (17.17) and (17.18) are flip sides of each other. If you take (17.17) and substitute it into (17.18), both sides become simply one.

G. The nature of the vacuum

Consider an experiment where we measure the electric and magnetic field of empty space. Surely, we would expect the result to be zero. However, in quantum mechanics, things can get more complicated. What would be the expectation value for these fields in the vacuum? Could they fluctuate from zero? To answer these questions, we would need the expectation values of the fields $\langle \mathbf{E}(\mathbf{r})\rangle$ and $\langle \mathbf{B}(\mathbf{r})\rangle$ and their squares $\langle \mathbf{E}^2(\mathbf{r})\rangle$ and $\langle \mathbf{B}^2(\mathbf{r})\rangle$. We start by computing $\mathbf{E}(\mathbf{r})|0\rangle$ and $\mathbf{B}(\mathbf{r})|0\rangle$, which work out to

$$\mathbf{E}(\mathbf{r})|0\rangle = -i\sum_{\mathbf{k},\sigma}\sqrt{\frac{\hbar\omega_k}{2\varepsilon_0 V}}\boldsymbol{\varepsilon}^*_{\mathbf{k}\sigma} e^{-i\mathbf{k}\cdot\mathbf{r}}|1,\mathbf{k},\sigma\rangle,$$

$$\mathbf{B}(\mathbf{r})|0\rangle = -i\sum_{\mathbf{k},\sigma}\sqrt{\frac{\hbar}{2\varepsilon_0 V\omega_k}}\mathbf{k}\times\boldsymbol{\varepsilon}^*_{\mathbf{k}\sigma} e^{-i\mathbf{k}\cdot\mathbf{r}}|1,\mathbf{k},\sigma\rangle.$$

We then immediately find $\langle 0|\mathbf{E}(\mathbf{r})|0\rangle = \langle 0|\mathbf{B}(\mathbf{r})|0\rangle = 0$. In contrast, we have

$$\langle 0|\mathbf{E}^2(\mathbf{r})|0\rangle = \left|\mathbf{E}(\mathbf{r})|0\rangle\right|^2 = \frac{\hbar}{2\varepsilon_0 V}\sum_{\mathbf{k}\sigma}\sum_{\mathbf{k}'\sigma'}\sqrt{\omega_k\omega_{k'}}\left(\boldsymbol{\varepsilon}_{\mathbf{k}\sigma}\cdot\boldsymbol{\varepsilon}^*_{\mathbf{k}'\sigma'}\right)e^{i\mathbf{k}\cdot\mathbf{r}-i\mathbf{k}'\cdot\mathbf{r}}\langle 1,\mathbf{k},\sigma|1,\mathbf{k}',\sigma'\rangle$$

$$= \frac{\hbar}{2\varepsilon_0 V}\sum_{\mathbf{k}\sigma}\omega_k = \frac{\hbar c}{\varepsilon_0 V}\sum_{\mathbf{k}} k = \frac{\hbar c}{\varepsilon_0}\int\frac{d^3\mathbf{k}}{(2\pi)^3}k,$$

$$\langle 0|\mathbf{B}^2(\mathbf{r})|0\rangle = \left|\mathbf{B}(\mathbf{r})|0\rangle\right|^2 = \frac{\hbar}{2\varepsilon_0 V}\sum_{\mathbf{k},\sigma}\sum_{\mathbf{k}',\sigma'}\frac{e^{i\mathbf{k}\cdot\mathbf{r}-i\mathbf{k}'\cdot\mathbf{r}}}{\sqrt{\omega_k\omega_{k'}}}\left(\mathbf{k}\times\boldsymbol{\varepsilon}_{\mathbf{k}\sigma}\right)\cdot\left(\mathbf{k}'\times\boldsymbol{\varepsilon}^*_{\mathbf{k}'\sigma'}\right)\langle 1,\mathbf{k},\sigma|1,\mathbf{k}',\sigma'\rangle$$

$$= \frac{\hbar}{2\varepsilon_0 V}\sum_{\mathbf{k},\sigma}\frac{\left|\mathbf{k}\times\boldsymbol{\varepsilon}_{\mathbf{k}\sigma}\right|^2}{\omega_k} = \frac{\hbar}{2\varepsilon_0 V}\sum_{\mathbf{k},\sigma}\frac{k^2}{\omega_k} = \frac{\hbar}{\varepsilon_0 V c}\sum_{\mathbf{k}} k = \frac{\hbar}{\varepsilon_0 c}\int\frac{d^3\mathbf{k}}{(2\pi)^3}k, \tag{17.19}$$

where at the last step, we went to the infinite volume limit. Surprisingly, even though the *average* value of the electric field and magnetic fields are finite, the expectation values of the *squares* are infinite, suggesting that the fields have large fluctuations. In retrospect, we probably should have anticipated this, since these two terms contribute to the energy density, and we already know that is infinite.

Experimentally, how come we don't notice this infinity? One reason is that it is impossible to measure the electric or magnetic field at exactly one point. Suppose that we use a probe of finite size, which measures not **E**(**r**), but rather

$$E_f(\mathbf{r}) \equiv \int f(\mathbf{s})\mathbf{E}(\mathbf{r}+\mathbf{s})\,d^3\mathbf{s}, \quad \text{where} \quad \int f(\mathbf{s})\,d^3\mathbf{s} = 1,$$

and $f(\mathbf{s})$ is concentrated in the neighborhood of zero.. Then we have

$$E_f(\mathbf{r})|0\rangle = -i\sum_{\mathbf{k}\sigma}\int f(\mathbf{s})\,d^3\mathbf{s}\,e^{-i\mathbf{k}\cdot(\mathbf{r}+\mathbf{s})}\boldsymbol{\varepsilon}^*_{\mathbf{k}\sigma}\sqrt{\frac{\hbar\omega_k}{2\varepsilon_0 V}}|1,\mathbf{k},\sigma\rangle\,.$$

Performing the **s** integral will then yield a Fourier transform of *f*, which yields a factor of 1 at long wavelength, but it will suppress the short wavelength contribution. Since real probes are always finite in size, this will reduce $\langle 0|\mathbf{E}_f^2(\mathbf{r})|0\rangle$ and $\langle 0|\mathbf{B}_f^2(\mathbf{r})|0\rangle$ and produce a finite value for the fluctuations. But it is always possible, at least in principle, to measure finite fluctuations in the field due to finite sized probes. Without going into too many details, the infinity also goes away if we average over time; the infinite contribution comes from very fast fluctuating fields, and realistic probes can simply not measure fluctuations that fast.

H. The Casimir effect

Before moving onwards, it is worth commenting again on the infinite energy density of the vacuum, which we can obtain easily from (17.19) substituted in (17.4) to yield

$$\langle 0|u(\mathbf{r})|0\rangle = \hbar c\int\frac{d^3\mathbf{k}}{(2\pi)^3}k\,. \qquad (17.20)$$

As we stated before, we can argue that since the only thing that matters is differences in energies, and this energy is there even in the vacuum, you can normally ignore this effect. There is, however, one important effect which requires that we consider this more carefully. Eq. (17.20) was obtained by considering the limit of infinite volume. What if we don't have infinite volume? Consider, for example, a parallel plate capacitor, consisting of two conductors very closely spaced together. We will assume the plates are each of area $A = L^2$, where L is very large compared to the separation a, as illustrated in Fig. 17-1. The area is assumed to be so large that it is effectively infinite, but the separation is small enough that the modes in this direction

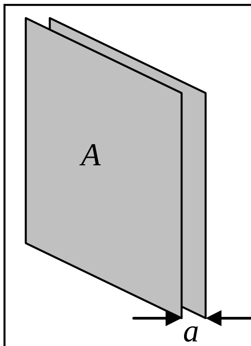


Figure 17-1: A parallel plate capacitor consisting of two conducting plates of area *A* separated by a small distance *a*.

will take on only distinctly discrete values. Therefore the energy density between the plates will not be given by (17.20). We must redo the work of section B, and quantize subject to these restrictions.

Considerable work is required to figure out what modes are allowed subject to our constraints. It is forbidden to have electric fields parallel to a conducting surface, which suggests that we should in general have $\mathbf{A}_{\parallel}\left(x,y,0,t\right)=\mathbf{A}_{\parallel}\left(x,y,a,t\right)=0$. Since virtually all modes have some component of **A** parallel to the conducting plates, this suggests we write

$$\mathbf{A}\left(\mathbf{r},t\right)=\sum_{\mathbf{k}}\mathbf{A}_{\mathbf{k}}\left(t\right)e^{ik_x x+ik_y y}\sin\left(k_z z\right), \tag{17.21}$$

The wave numbers are now restricted to be of the form

$$\mathbf{k}=\left(\frac{2\pi n_x}{L},\frac{2\pi n_y}{L},\frac{\pi n_z}{a}\right), \tag{17.22}$$

where n_x and n_y are arbitrary integers, but n_z must be a positive integer. However, there is one other type of mode that we have missed in (17.21), which occurs because if **k** is parallel to the capacitor plates, we can choose our polarization $\boldsymbol{\varepsilon}=\hat{\mathbf{z}}$, perpendicular to the capacitor plates. This leads to additional terms of the form $A_{\mathbf{k}}\left(t\right)\hat{\mathbf{z}}e^{ik_x x+ik_y y}$, where $k_z=0$. Hence each value of **k** given in (17.22) with positive n_z will have two possible polarizations, but there will be a single additional polarization with $n_z = 0$.

Now, our Hamiltonian will still be given by (17.12), and therefore the ground state energy will be $E_0\left(a\right)=\frac{1}{2}\hbar c\sum_{\mathbf{k},\sigma}k$. In the usual manner, we can turn the k_x and k_y sums into integrals by taking the limit $L\to\infty$, but the k_z and polarization sum must be dealt with explicitly and we find

$$E_0\left(a\right)=L^2\sum_{k_z,\sigma}\int\frac{dk_x dk_y}{\left(2\pi\right)^2}\tfrac{1}{2}\hbar ck\,.$$

Not surprisingly, this number is infinite. However, we are interested in the *difference* between this value and the empty space vacuum value, which can be found by multiplying the energy density (17.20) by the volume L^2a, so we have

$$\Delta E\equiv E_0\left(a\right)-E_0=\tfrac{1}{2}\hbar cL^2\sum_{k_z,\sigma}\int\frac{dk_x dk_y}{\left(2\pi\right)^2}k-L^2a\hbar c\int\frac{d^3\mathbf{k}}{\left(2\pi\right)^3}k\,. \tag{17.23}$$

Now, we have a problem in that both expressions are infinite, and we don't know how to subtract them. Fortunately, this infinity is not physical, because real conductors do not work at arbitrarily high frequencies. Hence we should put in some sort of cutoff function $f(k)$ that is one for small k and vanishes for large k. The exact form used can be shown not to matter, so I will use the simple formula $f\left(k\right)=e^{-\beta k}$, where β is some small number, governing when the conductor effectively becomes transparent. Substituting this into (17.23), we have

$$\Delta E = \tfrac{1}{2} L^2 \hbar c \sum_{k_z,\sigma} \int \frac{dk_x dk_y}{(2\pi)^2} k e^{-\beta k} - L^2 a \hbar c \int \frac{d^3\mathbf{k}}{(2\pi)^3} k e^{-\beta k} .$$

On the first term, we switch first to cylindrical coordinates $k_\parallel^2 = k_x^2 + k_y^2$ and angle ϕ, perform the ϕ integral, and then switch to the spherical coordinate $k^2 = k_\parallel^2 + k_z^2$. In the latter term, we switch to spherical coordinates and perform all integrals. The result is

$$\Delta E = \frac{L^2 \hbar c}{4\pi} \sum_{k_z,\sigma} \int_0^\infty k_\parallel dk_\parallel k e^{-\beta k} - \frac{L^2 a \hbar c}{2\pi^2} \int_0^\infty k^2 k e^{-\beta k} dk = \frac{L^2 \hbar c}{4\pi} \sum_{k_z,\sigma} \int_{k_z}^\infty k^2 e^{-\beta k} dk - \frac{3L^2 a \hbar c}{\pi^2 \beta^4}$$

$$= \frac{L^2 \hbar c}{2\pi} \sum_{k_z,\sigma} \left[\frac{k_z^2}{2\beta} + \frac{k_z}{\beta^2} + \frac{1}{\beta^3} \right] e^{-\beta k_z} - \frac{3L^2 a \hbar c}{\pi^2 \beta^4} .$$

It's time to do the sums on k_z. As argued above, $k_z = \pi n / a$, where n is an integer. There will be two polarizations when n is positive, and one when $n = 0$, so we have

$$\Delta E = \frac{L^2 \hbar c}{2\pi} \left[\frac{1}{\beta^3} + \sum_{n=1}^\infty \left(\frac{\pi^2 n^2}{\beta a^2} + \frac{2\pi n}{\beta^2 a} + \frac{2}{\beta^3} \right) e^{-\pi n \beta / a} \right] - \frac{3L^2 a \hbar c}{\pi^2 \beta^4} . \qquad (17.25)$$

All the sums can be performed exactly using the identities

$$\sum_{n=1}^\infty x^n = \frac{x}{1-x}, \quad \sum_{n=1}^\infty n x^n = \frac{x}{(1-x)^2}, \quad \sum_{n=1}^\infty n^2 x^n = \frac{x + x^2}{(1-x)^3},$$

valid for $|x| < 1$. The first is just the geometric series, and the other two can be easily derived by taking the derivative of the previous series with respect to x. Applying these equations to (17.25), we see that

$$\Delta E = \frac{L^2 \hbar c}{2\pi} \left[\frac{\pi^2 \left(e^{-\pi\beta/a} + e^{-2\pi\beta/a} \right)}{a^2 \beta \left(1 - e^{-\pi\beta/a}\right)^3} + \frac{2\pi e^{-\pi\beta/a}}{a \beta^2 \left(1 - e^{-\pi\beta/a}\right)} + \frac{2 e^{-\pi\beta/a}}{\beta^3 \left(1 - e^{-\pi\beta/a}\right)} + \frac{1}{\beta^3} \right] - \frac{3L^2 a \hbar c}{\pi^2 \beta^4},$$

Now, the actual frequencies at which the cutoff occurs tend to correspond to wavelengths much shorter than the experimental separation we can achieve, so $\beta \ll a$. We therefore expand ΔE in this limit. Rewrite our expression in terms of $w = \pi\beta / 2a$.

$$\Delta E = \frac{\pi^2 L^2 \hbar c}{16 a^3} \left(\frac{\cosh w}{w \sinh^3 w} + \frac{1}{w^2 \sinh^2 w} + \frac{\cosh w}{w^3 \sinh w} - \frac{3}{w^4} \right).$$

We now expand in powers of w. We'll let Maple do the work for us:

```
> series(cosh(w)/w/sinh(w)^3 + 1/w^2/sinh(w)^2
  + cosh(w)/w^3/sinh(w) - 3/w^4,w,11);
```

$$\Delta E = \frac{\pi^2 L^2 \hbar c}{16 a^3} \left(-\tfrac{1}{45} + \tfrac{4}{315} w^2 - \tfrac{1}{315} w^4 + \cdots \right) = -\frac{\pi^2 L^2 \hbar c}{720 a^3} \left[1 + O\left(w^2\right) \right].$$

We see that the in the limit $w \to 0$ the energy difference is finite and non-zero. Not surprisingly, the energy is proportional to the area, so we actually have a formula for the energy per unit area. Note that the result is negative, so there is less energy as the plates draw closer. This means there is an attractive force between them, or rather, a force per unit area (pressure) given by

$$P = -\frac{1}{L^2}\frac{d}{da}(\Delta E) = -\frac{\pi^2 \hbar c}{240 a^4} = -\frac{1.30\ \text{mN/m}^2}{(a/\mu\text{m})^4}.$$

This force is attractive, pulling the two plates of the capacitor towards each other. Though small, it has been measured.

Problems for Chapter 17

1. In class, we quantized the free electromagnetic field. In homework, you will quantize the free massive scalar field, with classical energy

$$E = \tfrac{1}{2}\int d^3\mathbf{r}\left\{\dot{\phi}^2(\mathbf{r},t) + c^2\left[\nabla\phi(\mathbf{r},t)\right]^2 + \mu^2\phi^2(\mathbf{r},t)\right\}$$

   This problem differs from the electromagnetic field in that: (i) there is no such thing as gauge choice; (ii) the field $\phi(\mathbf{r},t)$ is not a vector field; it doesn't have components, and (iii) there is a new term $\mu^2\phi^2$, unlike anything you've seen before.

   a) Write such a classical field $\phi(\mathbf{r},t)$ in terms of Fourier modes $\phi_{\mathbf{k}}(t)$. What is the relationship between $\phi_{\mathbf{k}}(t)$ and $\phi_{-\mathbf{k}}(t)$?
   b) Substitute your expression for $\phi(\mathbf{r},t)$ into the expression for *E*. Work in finite volume *V* and do as many integrals and sums as possible.
   c) Restrict the sum using *only* positive values of **k**. Argue that you now have a sum of classical complex harmonic oscillators. What is the formula for $\omega_{\mathbf{k}}$, the frequency for each of these oscillators?
   d) Reinterpret *H* as a Hamiltonian, and quantize the resulting theory. Find an expression for the Hamiltonian in terms of creation and annihilation operators.

2. How do we create the classical analog of a plane wave quantum mechanically? Naively, you simply use a large number of quanta.
   a) Suppose the EM field is in the quantum state $|n,\mathbf{k},\sigma\rangle$, where *n* is large. Find the expectation value of the electric $\langle\mathbf{E}(\mathbf{r})\rangle$ and magnetic fields $\langle\mathbf{B}(\mathbf{r})\rangle$ for this quantum state. For definiteness, choose $\mathbf{k} = k\hat{\mathbf{z}}$ and $\boldsymbol{\varepsilon}_{\mathbf{k}\sigma} = \hat{\mathbf{x}}$
   b) Now try a coherent state, given by $|\psi_c\rangle = e^{-|c|^2/2}\sum_{n=0}^{\infty}\left(c^n/\sqrt{n!}\right)|n,\mathbf{k},\sigma\rangle$, where *c* is an arbitrary complex number. Once again, find the expectation value of the electric and magnetic field. Coherent states were described in section 5D.

3. Suppose we measure the instantaneous electric field using a probe of finite size, so that we actually measure $\mathbf{E}_f(\mathbf{r}) \equiv \int \mathbf{E}(\mathbf{r}+\mathbf{s}) f(\mathbf{s})\, d^3\mathbf{s}$, where $f(\mathbf{s}) = \pi^{-3/2} a^{-3} e^{-\mathbf{s}^2/a^2}$, where *a* is the characteristic size of the probe. For the vacuum state, find the expectation value of $\langle \mathbf{E}_f(\mathbf{r}) \rangle$ and $\langle \mathbf{E}_f^2(\mathbf{r}) \rangle$. You should take the infinite volume limit, and make sure your answer is independent of *V*.

4. Define, for the electric and magnetic field, the annihilation and creation parts as

$$\mathbf{E}_-(\mathbf{r}) = i\sum_{\mathbf{k},\sigma} \sqrt{\frac{\hbar\omega_k}{2\varepsilon_0 V}} \boldsymbol{\varepsilon}_{\mathbf{k}\sigma} e^{i\mathbf{k}\cdot\mathbf{r}} a_{\mathbf{k}\sigma}, \qquad \mathbf{E}_+(\mathbf{r}) = -i\sum_{\mathbf{k}\sigma} \sqrt{\frac{\hbar\omega_k}{2\varepsilon_0 V}} \boldsymbol{\varepsilon}^*_{\mathbf{k}\sigma} e^{-i\mathbf{k}\cdot\mathbf{r}} a^\dagger_{\mathbf{k}\sigma},$$

$$\mathbf{B}_-(\mathbf{r}) = i\sum_{\mathbf{k},\sigma} \sqrt{\frac{\hbar}{2\varepsilon_0 V\omega_k}} \mathbf{k}\times\boldsymbol{\varepsilon}_{\mathbf{k}\sigma} e^{i\mathbf{k}\cdot\mathbf{r}} a_{\mathbf{k}\sigma}, \quad \mathbf{B}_+(\mathbf{r}) = -i\sum_{\mathbf{k},\sigma} \sqrt{\frac{\hbar}{2\varepsilon_0 V\omega_k}} \mathbf{k}\times\boldsymbol{\varepsilon}^*_{\mathbf{k}\sigma} e^{-i\mathbf{k}\cdot\mathbf{r}} a^\dagger_{\mathbf{k}\sigma}.$$

It should be obvious that $\mathbf{E}(\mathbf{r}) = \mathbf{E}_+(\mathbf{r}) + \mathbf{E}_-(\mathbf{r})$ and $\mathbf{B}(\mathbf{r}) = \mathbf{B}_+(\mathbf{r}) + \mathbf{B}_-(\mathbf{r})$.

(a) Define the normal-ordered energy density as

$$\tilde{u}(\mathbf{r}) \equiv \tfrac{1}{2}\varepsilon_0 \left\{ \left[\mathbf{E}_+^2(\mathbf{r}) + 2\mathbf{E}_+(\mathbf{r})\cdot\mathbf{E}_-(\mathbf{r}) + \mathbf{E}_-^2(\mathbf{r}) \right] + c^2 \left[\mathbf{B}_+^2(\mathbf{r}) + 2\mathbf{B}_+(\mathbf{r})\cdot\mathbf{B}_-(\mathbf{r}) + \mathbf{B}_-^2(\mathbf{r}) \right] \right\}$$

Prove that this normal-ordered energy density differs from the usual definition by a constant, i.e., that the difference contains no operators (the constant will be infinite).

(b) Prove that the expectation value of this operator for the vacuum is zero.

(c) Consider the quantum state $|\psi\rangle = \frac{\sqrt{8}}{3}|0\rangle + \frac{1}{3}|2,\mathbf{q},\tau\rangle$; i.e., a quantum superposition of the vacuum and a two photon state with wave number $\mathbf{q}$ and polarization τ. To keep things simple, let the polarization $\boldsymbol{\varepsilon}_{\mathbf{q}\tau}$ be real. Work out the expectation value $\langle \tilde{u}(\mathbf{r}) \rangle$ for this quantum state.

(d) Sketch $\langle \tilde{u}(\mathbf{r}) \rangle$ as a function of $\mathbf{q}\cdot\mathbf{r}$. Note that it is sometimes negative (less energy than the vacuum!). Find its integral over space, and check that it does, however, have total energy positive.

XVIII. Photons and Atoms

We have quantized the electromagnetic field, and we have discussed atoms as well in terms of quantum mechanics. It is time to put our knowledge together so that we can gain an understanding of how photons interact with matter. Our tool will be primarily time-dependent perturbation theory, in which we divide the Hamiltonian H into two pieces, $H = H_0 + W$, where H_0 will be assumed to be solved, and W will be small. The rate at which an interaction occurs is then given by Fermi's Golden rule, (15.35), and the transition matrix (15.34), given by

$$\mathcal{T}_{FI} = W_{FI} + \lim_{\varepsilon\to 0^+}\left[\sum_m \frac{W_{Fm}W_{mI}}{\left(E_I - E_m + i\varepsilon\right)} + \sum_m\sum_n \frac{W_{Fm}W_{mn}W_{nI}}{\left(E_I - E_n + i\varepsilon\right)\left(E_I - E_m + i\varepsilon\right)} + \cdots\right],$$

$$\Gamma\left(I \to F\right) = 2\pi\hbar^{-1}\left|\mathcal{T}_{FI}\right|^2 \delta\left(E_F - E_I\right), \tag{18.1}$$

where $W_{nm} = \langle n|W|m\rangle$. Our first step will be to break the Hamiltonian up into a main part and a perturbation, and find the eigenstates of the main part.

A. The Hamiltonian

The Hamiltonian we wish to consider is one involving both atoms and (quantized) electromagnetic fields. The pure electromagnetic field energy H_{em} will be given by (17.5), which, after quantization, becomes (17.15). This Hamiltonian was the focus of the previous chapter. In addition, there will be the interaction of all the electrons in all of the atoms, etc. With the help of (9.20), we see that the full Hamiltonian will be

$$H = \sum_{j=1}^{N}\left\{\frac{1}{2m}\left[\mathbf{P}_j + e\mathbf{A}\left(\mathbf{R}_j\right)\right]^2 + \frac{e}{m}\mathbf{B}\left(\mathbf{R}_j\right)\cdot\mathbf{S}_j\right\} + V\left(\mathbf{R}_1,\ldots,\mathbf{R}_N\right) + H_{em}.$$

where V contains all of the interactions of the electrons with each other, or with the nuclei or background fields, etc., and we have approximated $g = 2$ for the electron. Indeed, in general we might want to also include lesser effects in V, such as the spin-orbit coupling within an atom, but what we want to *exclude* is any interaction with external electromagnetic fields, which are explicitly shown. Keep in mind that **A** and **B** are no longer mere functions (as they were previously) but now are full operators. Recall that we are working in Coulomb gauge, and therefore the electrostatic potential is determined by the instantaneous charge distribution.

We now wish to divide H up into "large" and "small" pieces, which we do as follows:

$$H = H_{\text{atom}} + H_{em} + W^{(1)} + W^{(2)},$$

where

$$H_{\text{atom}} = \sum_{j=1}^{N} \frac{1}{2m}\mathbf{P}_j^2 + V\left(\mathbf{R}_1,\ldots,\mathbf{R}_N\right),$$

and the perturbations are[1]

$$W^{(1)} = \frac{e}{m}\sum_{j=1}^{N}\left[\mathbf{A}\left(\mathbf{R}_j\right)\cdot\mathbf{P}_j + \mathbf{B}\left(\mathbf{R}_j\right)\cdot\mathbf{S}_j\right] \quad \text{and} \quad W^{(2)} = \frac{e^2}{2m}\sum_{j=1}^{N}\mathbf{A}^2\left(\mathbf{R}_j\right). \qquad (18.2)$$

This distinction between the two perturbative terms is a natural one, because $W^{(1)}$ is first order in the charge *e*, while $W^{(2)}$ is second order, and one way we will keep track of our perturbation theory is by counting factors of *e*. Hence if we perform a computation to second order, we will allow up to two factors of $W^{(1)}$, but only one factor of $W^{(2)}$. The explicit form of (18.2) will be needed later in terms of creation and annihilation operators, and using (17.13) and (17.14b), these can be written

$$W^{(1)} = \frac{e}{m}\sum_{j=1}^{N}\sum_{\mathbf{k}\sigma}\sqrt{\frac{\hbar}{2\varepsilon_0 V\omega_k}}\left\{e^{i\mathbf{k}\cdot\mathbf{R}_j}\boldsymbol{\varepsilon}_{\mathbf{k}\sigma}\cdot\left[\mathbf{P}_j + i\left(\mathbf{S}_j\times\mathbf{k}\right)\right]a_{\mathbf{k}\sigma} + e^{-i\mathbf{k}\cdot\mathbf{R}_j}\boldsymbol{\varepsilon}_{\mathbf{k}\sigma}^*\cdot\left[\mathbf{P}_j - i\left(\mathbf{S}_j\times\mathbf{k}\right)\right]a_{\mathbf{k}\sigma}^\dagger\right\},$$

$$W^{(2)} = \frac{e^2\hbar}{4m\varepsilon_0 V}\sum_{j=1}^{N}\sum_{\mathbf{k}\sigma}\sum_{\mathbf{k}'\sigma'}\frac{\left(e^{i\mathbf{k}\cdot\mathbf{R}_j}\boldsymbol{\varepsilon}_{\mathbf{k}\sigma}a_{\mathbf{k}\sigma} + e^{-i\mathbf{k}\cdot\mathbf{R}_j}\boldsymbol{\varepsilon}_{\mathbf{k}\sigma}^*a_{\mathbf{k}\sigma}^\dagger\right)\cdot\left(e^{i\mathbf{k}'\cdot\mathbf{R}_j}\boldsymbol{\varepsilon}_{\mathbf{k}'\sigma}a_{\mathbf{k}'\sigma} + e^{-i\mathbf{k}'\cdot\mathbf{R}_j}\boldsymbol{\varepsilon}_{\mathbf{k}'\sigma'}^*a_{\mathbf{k}'\sigma'}^\dagger\right)}{\sqrt{\omega_k\omega_{k'}}}.$$

(18.3)

We now let our first two terms be our unperturbed Hamiltonian,

$$H_0 = H_{\text{atom}} + H_{em}.$$

Fortunately, these two terms are completely decoupled, and therefore to find eigenstates of H_0, we need only find eigenstates of these two parts separately. We will now assume that we have somehow managed to find the exact eigenstates of H_{atom}, which we call $\left|\phi_n\right\rangle$, where *n* describes all the quantum numbers associated with the atom itself, such as *l*, *j*, m_j, etc. This state will have energy ε_n. In addition, there will be eigenstates of H_{em}, which we computed in the previous chapter. The overall eigenstates will then be given by

$$\left|\phi_n; n_1, \mathbf{k}_1, \sigma_1; n_2, \mathbf{k}_2, \sigma_2; \ldots; n_M, \mathbf{k}_M, \sigma_M\right\rangle.$$

and will have energy

$$E = \varepsilon_n + \hbar\left(n_1\omega_1 + n_2\omega_2 + \cdots + n_M\omega_M\right).$$

We are now ready to start putting in the effect of our perturbations.

---

[1] Note that $\mathbf{P}_j\cdot\mathbf{A}\left(\mathbf{R}_j\right) = \mathbf{A}\left(\mathbf{R}_j\right)\cdot\mathbf{P}_j$, because we are working in Coulomb gauge where $\nabla\cdot\mathbf{A}\left(\mathbf{r}\right) = 0$.

B. Absorption and Emission of Photons by Atoms

Consider first the effect of our interaction terms to leading order in e. To this order, we need only consider $W^{(1)}$, given in (18.3). We immediately note that this perturbation can only create or destroy one photon. It follows that the final state must be identical with the initial state, save for a single photon. The only matrix elements we will consider, therefore, will be of the form

$$\left\langle \phi_F ; n_1 \pm 1, \mathbf{k}_1, \sigma_1 ; \ldots \right| W^{(1)} \left| \phi_I ; n_1, \mathbf{k}_1, \sigma_1 ; \ldots \right\rangle .$$

The energy difference $E_F - E_I$ will therefore be

$$\begin{aligned} E_F - E_I &= \varepsilon_F + \hbar\left[\left(n_1 \pm 1\right)\omega + n_2\omega_2 + \cdots + n_M\omega_M\right] - \varepsilon_I - \hbar\left[n_1\omega + n_2\omega_2 + \cdots + n_M\omega_M\right] \\ &= \varepsilon_F - \varepsilon_I \pm \hbar\omega = \hbar\left(\omega_{FI} \pm \omega\right), \end{aligned}$$

where we have renamed $\omega_1 = \omega$ since this is the frequency that will interest us most. Since this must vanish by Fermi's Golden rule, we conclude that $\varepsilon_F - \varepsilon_I = \mp\hbar\omega$, so we either emit a photon and decrease the atom's energy, or we absorb a photon and increase the atom's energy.

Consider first the case where we absorb a photon, so that $\varepsilon_F > \varepsilon_I$. Then only the annihilation part of $W^{(1)}$ will contribute. Furthermore, in the sum, only the single term that matches the wave number $\mathbf{k}_1$ and polarization σ_1 will contribute. We will rename these as $\mathbf{k}$ and σ, so we have

$$W_{FI}^{(1)} = \frac{e}{m}\sum_{j=1}^{N}\sqrt{\frac{\hbar}{2\varepsilon_0 V\omega}}\left\langle \phi_F ; n-1, \mathbf{k}, \sigma ; \ldots \right| e^{i\mathbf{k}\cdot\mathbf{R}_j}\boldsymbol{\varepsilon}_{\mathbf{k}\sigma}\cdot\left[\mathbf{P}_j + i\left(\mathbf{S}_j \times \mathbf{k}\right)\right] a_{\mathbf{k}\sigma}\left| \phi_I ; n, \mathbf{k}, \sigma ; \ldots \right\rangle .$$

The photon part of this expression is easy to find; it is just

$$\left\langle n-1, \mathbf{k}, \sigma ; \ldots \right| a_{\mathbf{k}\sigma} \left| n, \mathbf{k}, \sigma ; \ldots \right\rangle = \sqrt{n}\left\langle n-1, \mathbf{k}, \sigma ; \ldots \middle| n-1, \mathbf{k}, \sigma ; \ldots \right\rangle = \sqrt{n} ,$$

so the whole matrix element is just

$$W_{FI}^{(1)} = \frac{e}{m}\sum_{j=1}^{N}\sqrt{\frac{\hbar n}{2\varepsilon_0 V\omega}}\left\langle \phi_F \right| e^{i\mathbf{k}\cdot\mathbf{R}_j}\boldsymbol{\varepsilon}\cdot\left[\mathbf{P}_j + i\left(\mathbf{S}_j \times \mathbf{k}\right)\right]\left| \phi_I \right\rangle . \qquad (18.4)$$

Comparing this, for example, with (15.25), we see that our computation now closely follows what we found before. To leading order, we can approximate $e^{i\mathbf{k}\cdot\mathbf{R}_j} = 1$, and ignore the spin term to obtain the electric dipole approximation

$$W_{FI}^{(1)} \approx \frac{e}{m}\sqrt{\frac{\hbar n}{2\varepsilon_0 V\omega}}\boldsymbol{\varepsilon}\cdot\left\langle \phi_F \right| \mathbf{P} \left| \phi_I \right\rangle .$$

In a manner identical to before, we can again derive equation (15.27), relating $\left\langle \phi_F \right| \mathbf{P} \left| \phi_I \right\rangle$ and $\left\langle \phi_F \right| \mathbf{R} \left| \phi_I \right\rangle$, and rewrite this as

$$W_{FI}^{(1)} \approx ie\sqrt{\frac{n\hbar\omega}{2\varepsilon_0 V}}\,\boldsymbol{\varepsilon}\cdot\langle\phi_F|\mathbf{R}|\phi_I\rangle = ie\sqrt{\frac{n\hbar\omega}{2\varepsilon_0 V}}\,\boldsymbol{\varepsilon}\cdot\mathbf{r}_{FI} \;.$$

where we used the fact that we must have $\omega = \omega_{FI}$. Substituting this into (18.1) then yields

$$\Gamma(I\to F) = \frac{\pi e^2 n\omega}{\varepsilon_0 V}\left|\boldsymbol{\varepsilon}\cdot\mathbf{r}_{FI}\right|^2 \delta\left(\varepsilon_F - \varepsilon_I - \hbar\omega\right) = 4\pi^2\alpha\hbar^{-1}\left(\frac{cn\hbar\omega}{V}\right)\left|\boldsymbol{\varepsilon}\cdot\mathbf{r}_{FI}\right|^2 \delta\left(\omega_{FI}-\omega\right),$$

where we have replaced factors of *e* using the fine structure constant $\alpha = e^2/4\pi\varepsilon_0\hbar c$. A careful comparison with (15.29) will convince you that they are identical formulas. The factor of $(cn\hbar\omega/V)$ is simply the energy of the photons $n\hbar\omega$, divided by the volume (yielding energy density) and multiplied by the speed of light, and hence is just the intensity $\mathcal{I}$.

Let's now consider the reverse case, where the final energy is less than the initial. Then we must increase the number of photons by one, which means we need the other half of our perturbation, so

$$W_{FI}^{(1)} = \frac{e}{m}\sum_{j=1}^{N}\sqrt{\frac{\hbar}{2\varepsilon_0 V\omega}}\left\langle\phi_F; n+1,\mathbf{k},\sigma;\ldots\right| e^{i\mathbf{k}\cdot\mathbf{R}_j}\left[\boldsymbol{\varepsilon}^*\cdot\mathbf{P}_j - i\left(\mathbf{k}\times\boldsymbol{\varepsilon}^*\right)\cdot\mathbf{S}_j\right] a_{\mathbf{k}\sigma}^\dagger\left|\phi_I; n,\mathbf{k},\sigma;\ldots\right\rangle.$$

This time the photon part of this matrix element is $\left\langle n+1,\mathbf{k},\sigma;\ldots\right| a_{\mathbf{k}\sigma}^\dagger \left| n,\mathbf{k},\sigma;\ldots\right\rangle = \sqrt{n+1}$, which yields

$$W_{FI}^{(1)} = \frac{e}{m}\sum_{j=1}^{N}\sqrt{\frac{\hbar(n+1)}{2\varepsilon_0 V\omega}}\left\langle\phi_F\right| e^{-i\mathbf{k}\cdot\mathbf{R}_j}\left[\boldsymbol{\varepsilon}^*\cdot\mathbf{P}_j - i\left(\mathbf{k}\times\boldsymbol{\varepsilon}^*\right)\cdot\mathbf{S}_j\right]\left|\phi_I\right\rangle.$$

In the dipole approximation, this can be simplified in a manner very similar to before. Skipping steps, the final answer is

$$\Gamma(I\to F) = \left(\frac{4\pi^2\alpha}{\hbar}\right)\left[\frac{c(n+1)\hbar\omega}{V}\right]\left|\boldsymbol{\varepsilon}^*\cdot\mathbf{r}_{FI}\right|^2\delta\left(\omega-\omega_{IF}\right).$$

This time, the result is *not* what we got before. If you keep the term proportional to *n*, we will get exactly the same result as before. The interesting thing is that we have a new term which does not require the presence of photons in the initial state at all. This new process is called *spontaneous emission*. The rate is given, in the electric dipole approximation, by

$$\Gamma(I\to F) = \frac{4\pi^2\alpha c\omega}{V}\left|\boldsymbol{\varepsilon}^*\cdot\mathbf{r}_{FI}\right|^2\delta\left(\omega-\omega_{IF}\right).$$

As it stands this formula is a bit difficult to interpret. It has a delta function, which makes it look infinite, but it also has the reciprocal of the volume, which just means that in the limit of infinite volume, the probability of it going to a particular wave number **k** is vanishingly small. The way to avoid these double difficulties is to sum over all possible outgoing wave numbers, and then take the limit of infinite volume, which gives us

$$\Gamma(I\to F)=\frac{4\pi^2\alpha c\omega}{V}\left|\boldsymbol{\varepsilon}^*\cdot\mathbf{r}_{FI}\right|^2\sum_{\mathbf{k}}\delta(\omega-\omega_{IF})=4\pi^2\alpha c\omega\int\frac{d^3\mathbf{k}}{(2\pi)^3}\left|\boldsymbol{\varepsilon}^*\cdot\mathbf{r}_{FI}\right|^2\delta(\omega-\omega_{IF})$$

$$=\frac{\alpha c\omega}{2\pi}\int d\Omega_k\left|\boldsymbol{\varepsilon}^*\cdot\mathbf{r}_{FI}\right|^2\int k^2dk\,\delta(kc-\omega_{IF})=\frac{\alpha\omega k^2}{2\pi}\int d\Omega_k\left|\boldsymbol{\varepsilon}^*\cdot\mathbf{r}_{FI}\right|^2,$$

$$\frac{d\Gamma(I\to F)}{d\Omega_k}=\frac{\alpha\omega_{IF}^3}{2\pi c^2}\left|\boldsymbol{\varepsilon}^*\cdot\mathbf{r}_{FI}\right|^2.$$

This rate is the angle-dependant polarized rate. If we do not measure the polarization of the outgoing wave, then the effective rate is the sum of this expression over the two polarizations. Without working through the details too much, the result is

$$\frac{d\Gamma(I\to F)}{d\Omega_k}=\frac{\alpha\omega_{IF}^3}{2\pi c^2}\left(\left|\mathbf{r}_{FI}\right|^2-\left|\hat{\mathbf{k}}\cdot\mathbf{r}_{FI}\right|^2\right).$$

where $\hat{\mathbf{k}}$ denotes a unit vector in the direction of $\mathbf{k}$. For example, if $\mathbf{r}_{FI}$ is a real vector, the last factor is simply $\sin^2\theta$, where θ is the angle between $\mathbf{k}$ and $\mathbf{r}_{FI}$. If we don't measure the direction of the final photon, we can integrate over solid angle to get a final answer

$$\Gamma(I\to F)=\frac{4\alpha\omega_{IF}^3\left|\mathbf{r}_{FI}\right|^2}{3c^2}. \tag{18.5}$$

Of course, we can go beyond the dipole approximation when needed. The atomic matrix elements can be expanded in powers of $\mathbf{k}\cdot\mathbf{R}_j$ to any order desired. The first three terms can be written in the form

$$\frac{e}{m}\left\langle\phi_F\right|e^{-i\mathbf{k}\cdot\mathbf{R}_j}\left[\boldsymbol{\varepsilon}^*\cdot\mathbf{P}_j-i\left(\mathbf{k}\times\boldsymbol{\varepsilon}^*\right)\cdot\mathbf{S}_j\right]\left|\phi_I\right\rangle=\left\langle\phi_F\right|\Big[ie\omega_{FI}\left(\boldsymbol{\varepsilon}^*\cdot\mathbf{R}_j\right)+\tfrac{1}{2}e\omega_{FI}\left(\boldsymbol{\varepsilon}^*\cdot\mathbf{R}_j\right)\left(\mathbf{k}\cdot\mathbf{R}_j\right)$$
$$-\frac{ie}{m}\left(\mathbf{k}\times\boldsymbol{\varepsilon}^*\right)\cdot\left(\mathbf{S}_j+\tfrac{1}{2}\mathbf{L}_j\right)+\cdots\Big]\left|\phi_I\right\rangle.$$

The three terms correspond to the electric dipole, electric quadrupole, and magnetic dipole terms respectively. Equations analogous to (18.5) can then be derived for each of these other two cases.

C. The Self-Energy of the Electron

We now see that to leading order in perturbation theory, $W^{(1)}$ causes atoms to absorb or emit a single photon. What is the effect of $W^{(2)}$? There are a variety of effects, but notice in particular that it will shift the energy of an arbitrary atomic state $|\phi\rangle$. To first order in time-independent perturbation theory, the shift in energy of a single electron will be $\varepsilon' = \langle\phi|W^{(2)}|\phi\rangle = e^2\langle\phi|\mathbf{A}^2(\mathbf{R})|\phi\rangle/2m$. We therefore compute

$$\mathbf{A}(\mathbf{R})|\phi\rangle = \sum_{\mathbf{k},\sigma}\sqrt{\frac{\hbar}{2\varepsilon_0\omega_k V}}\left(e^{i\mathbf{k}\cdot\mathbf{R}}a_{\mathbf{k}\sigma}\boldsymbol{\varepsilon}_{\mathbf{k}\sigma} + e^{-i\mathbf{k}\cdot\mathbf{R}}a^\dagger_{\mathbf{k}\sigma}\boldsymbol{\varepsilon}^*_{\mathbf{k}\sigma}\right)|\phi\rangle = \sum_{\mathbf{k},\sigma}\sqrt{\frac{\hbar}{2\varepsilon_0\omega_k V}}e^{-i\mathbf{k}\cdot\mathbf{R}}\boldsymbol{\varepsilon}^*_{\mathbf{k}\sigma}|\phi;1,\mathbf{k},\sigma\rangle .$$

We therefore have

$$\varepsilon' = \frac{e^2}{2m}\langle\phi|\mathbf{A}^2(\mathbf{R})|\phi\rangle = \frac{\hbar e^2}{4m\varepsilon_0 V}\sum_{\mathbf{k},\sigma}\sum_{\mathbf{k},\sigma'}\frac{\boldsymbol{\varepsilon}_{\mathbf{k}\sigma}\cdot\boldsymbol{\varepsilon}^*_{\mathbf{k}'\sigma'}}{\sqrt{\omega_k\omega_{k'}}}\langle\phi;1,\mathbf{k},\sigma|e^{i\mathbf{k}'\cdot\mathbf{R}}e^{-i\mathbf{k}\cdot\mathbf{R}}|\phi;1,\mathbf{k}',\sigma'\rangle$$

$$= \frac{\hbar e^2}{4m\varepsilon_0 V}\sum_{\mathbf{k},\sigma}\frac{1}{\omega_k} = \frac{\hbar e^2}{2m\varepsilon_0}\int\frac{d^3\mathbf{k}}{(2\pi)^3\omega_k} = \frac{\hbar e^2}{2m\varepsilon_0}\frac{4\pi}{(2\pi)^3}\int_0^\infty\frac{k^2dk}{ck} = \frac{\alpha\hbar^2}{\pi m}\int_0^\infty k\,dk = \infty .$$

Hence the electron will be shifted up in energy by an infinite amount! Note, however, that this shift is completely independent of what state the electron is in. It is therefore an intrinsic property of the electron, and is irrelevant.

It is sometimes suggested that these infinities that seem to be appearing have something inherent to do with quantum mechanics. But the same problems plague classical mechanics. An electron at the origin is surrounded by an electric field $\mathbf{E}(\mathbf{r}) = k_e e\hat{\mathbf{r}}/r^2$, which has an energy density $\frac{1}{2}\varepsilon_0\mathbf{E}^2(\mathbf{r}) = k_e e^2/8\pi r^4 = \alpha\hbar c/8\pi r^4$. If we integrate the resulting energy density over all space, we find there is an infinite energy associated with the electric field around an electron. Hence this problem of infinities exists classically as well.

D. Photon Scattering

We turn our attention now to the subject of photon scattering. We will consider situations where both the initial and final state includes a photon. We will assume only a single photon, so the initial and final states are

$$|I\rangle = |\phi_I;\mathbf{k}_I,\sigma_I\rangle \quad\text{and}\quad |F\rangle = |\phi_F;\mathbf{k}_F,\sigma_F\rangle ,$$

where there is an implied "1" describing the number of photons in each case. The initial and final state energy are $E_I = \varepsilon_I + \hbar\omega_I$ and $E_F = \varepsilon_F + \hbar\omega_F$. We are interested only in the case where the final photon differs from the initial one. We would like to calculate the probability $P(I\to F)$ to second order in perturbation theory. The amplitude is

$$\mathcal{T}_{FI} = \langle F|W^{(2)}|I\rangle + \lim_{\delta\to 0^+}\sum_m\frac{\langle F|W^{(1)}|m\rangle\langle m|W^{(1)}|I\rangle}{E_I - E_m + i\delta} , \qquad (18.6)$$

where we have changed our small variable to δ to avoid confusion with the atomic energies ε_m. We have left out $W^{(1)}$ in the first term because it can only create or annihilate one photon, and therefore $\langle F | W^{(1)} | I \rangle = 0$. We have left out $W^{(2)}$ in the second term because this has more factors of the coupling *e*, and therefore is higher order.

In the second term, what sort of intermediate states are possible? Since we have assumed the final photon state is distinct from the initial, and each of the two perturbations can only annihilate or create one photon, we conclude that one factor of $W^{(1)}$ must be eliminating the initial photon and the other creating the final photon. Depending on which is which, the intermediate state will either have no photons in it, or it will have two photons, one each in the initial and final state. So the only possibilities for the intermediate state are $|m\rangle = |\phi_m\rangle$ or $|m\rangle = |\phi_m; \mathbf{k}_I, \sigma_I; \mathbf{k}_F, \sigma_F\rangle$. These states have energies of $E_m = \varepsilon_m$ or $E_m = \varepsilon_m + \hbar\omega_I + \hbar\omega_F$. Thus the sum in (18.6) will become a double sum, one term for each of these cases, and we have

$$\mathcal{T}_{FI} = \langle \phi_F; \mathbf{k}_F, \sigma_F | W^{(2)} | \phi_I; \mathbf{k}_I, \sigma_I \rangle + \lim_{\delta \to 0^+} \sum_m \left\{ \frac{\langle \phi_F; \mathbf{k}_F, \sigma_F | W^{(1)} | \phi_m \rangle \langle \phi_m | W^{(1)} | \phi_I; \mathbf{k}_I, \sigma_I \rangle}{\varepsilon_I - \varepsilon_m + \hbar\omega_I + i\delta} \right.$$
$$\left. + \frac{\langle \phi_F; \mathbf{k}_F, \sigma_F | W^{(1)} | \phi_m; \mathbf{k}_I, \sigma_I; \mathbf{k}_F, \sigma_F \rangle \langle \phi_m; \mathbf{k}_I, \sigma_I; \mathbf{k}_F, \sigma_F | W^{(1)} | \phi_I; \mathbf{k}_I, \sigma_I \rangle}{\varepsilon_I - \varepsilon_m - \hbar\omega_F + i\delta} \right\}. \quad (18.7)$$

We now turn our attention to evaluating and using (18.7) in certain special cases, but before we go on, it is helpful to come up with a more compact notation to keep track of what is going on. When necessary, we will refer to the three terms in (18.7) as $\mathcal{T}_{FI}(1)$, $\mathcal{T}_{FI}(2)$, and $\mathcal{T}_{FI}(3)$ respectively.

E. A Diagrammatic Approach

When the expressions are getting as complicated as (18.7) it is a good idea to try to come up with an easier way to keep track of what is going on. Fortunately, there is a neat diagrammatic notation that helps us understand what is happening. In this notation, an electron (or atom) will be denoted by a solid line with an arrow on it, and a photon by a wiggly line. Time will increase from left to right, and interactions will be denoted by a dot. For example, $W^{(1)}$ can create or annihilate one photon, and there are correspondingly two corresponding diagrams, as illustrated in Fig. 18-1. In contrast, $W^{(2)}$ can either create two photons, annihilate two photons, or create and annihilate one of each. Hence there are three corresponding diagrams, as illustrated in Fig. 18-2.

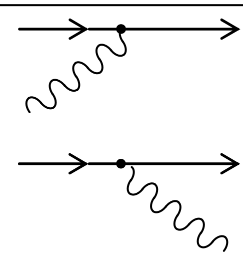


Figure 18-1: The two diagrams corresponding to the interactions $W^{(1)}$.

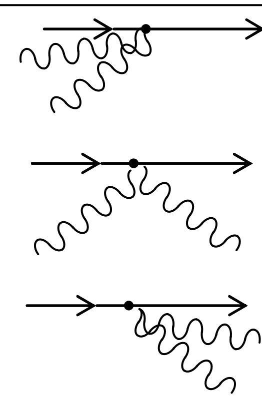
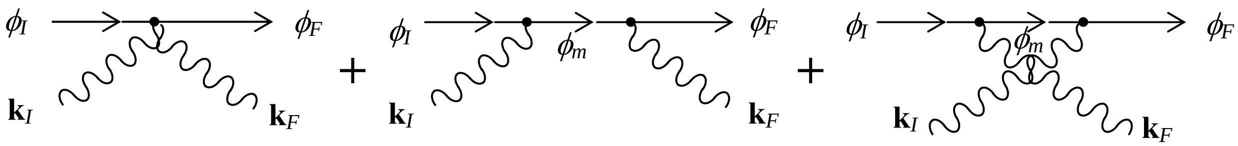


Figure 18-2: The three diagrams corresponding to the interaction $W^{(2)}$.

An equation like (18.7) could be written in the simple diagrammatic notation as:



We see that in the first diagram, the photons are emitted and reabsorbed at the same place and time ($W^{(2)}$), while in the other two diagrams, there are two factors of $W^{(1)}$. By looking at the diagrams half way through we can see that the intermediate state contains only an atom in the middle diagram, but there is an atom and two photons in the intermediate state in the final diagram.

F. Thomson Scattering

As our first computation of this process, consider a free electron, for which the "atomic" Hamiltonian is simply given by $H_{\text{atom}} = \mathbf{P}^2/2m$. The eigenstates of this Hamiltonian will be proportional to $e^{i\mathbf{q}\cdot\mathbf{r}}$, and since we are working in finite volume, we can normalize them simply as $\phi_{\mathbf{p}}(\mathbf{r}) = e^{i\mathbf{q}\cdot\mathbf{r}}/\sqrt{V}$. Hence our initial state will be labeled $|I\rangle = |\mathbf{q}_I;\mathbf{k}_I,\sigma_I\rangle$. For definiteness, and to keep our computations simple, we will assume the initial electron is at rest, so $\mathbf{q}_I = 0$.[1]

Which of the three terms in (18.7) will be most important? The first one, $\mathcal{T}_{FI}(1)$, has a matrix element of $W^{(2)} = e^2\mathbf{A}^2/2m$. The second and third term each have factors that looks like $e\mathbf{A}\cdot\mathbf{P}/m$ and $e\mathbf{B}\cdot\mathbf{S}/m$. Because we chose the initial state to have momentum zero, it is easy to see that **P** vanishes in the second factor of each of the second and third terms. Hence we must look at $e\mathbf{B}\cdot\mathbf{S}/m$. The eigenvalues of **S** are of order $\hbar$, while $\mathbf{B} = \nabla\times\mathbf{A}$ which will turn into a factor of $\mathbf{k}\times\mathbf{A}$, where **k** is the wave number of one of the photons. The first factor has a similar term. Noting that the energy denominators contain terms like $\hbar\omega$, we therefore estimate the order of magnitude of the second and third terms in (18.7) as

$$\mathcal{T}_{FI}(2) \sim \mathcal{T}_{FI}(3) \sim \frac{e^2\hbar^2\mathbf{A}^2k^2}{\hbar\omega m^2}$$

The relative size of these compared to the first term is therefore of order

$$\frac{\mathcal{T}_{FI}(2)}{\mathcal{T}_{FI}(1)} \sim \frac{\mathcal{T}_{FI}(3)}{\mathcal{T}_{FI}(1)} \sim \frac{\hbar k^2}{\omega m} = \frac{\hbar\omega}{mc^2}$$

Thus the second and third terms will be dominated by the first if the photons have an energy small compared to the rest energy of the electron. Indeed, if this is *not* the case,

[1] This simplifies the computation, but does not affect the answer.

then we need to consider relativistic corrections for the electron, and our entire formalism is wrong. We therefore ignore $\mathcal{T}_{FI}(2)$, and $\mathcal{T}_{FI}(3)$ and have

$$\mathcal{T}_{FI} = \mathcal{T}_{FI}(1) = \left\langle \mathbf{q}_F;\mathbf{k}_F,\sigma_F \left| W^{(2)} \right| \mathbf{q}_I;\mathbf{k}_I,\sigma_I \right\rangle = \frac{e^2}{2m}\left\langle \mathbf{q}_F;\mathbf{k}_F,\sigma_F \left| \mathbf{A}^2(\mathbf{R}) \right| \mathbf{q}_I;\mathbf{k}_I,\sigma_I \right\rangle$$

$$= \frac{e^2}{2m}\sum_{\mathbf{k}\sigma}\sum_{\mathbf{k}'\sigma'}\frac{\hbar}{2\varepsilon_0 V\sqrt{\omega_k\omega_{k'}}}\left[\begin{array}{l}\left\langle \mathbf{q}_F;\mathbf{k}_F,\sigma_F \right|\left(e^{i\mathbf{k}\cdot\mathbf{R}}a_{\mathbf{k}\sigma}\boldsymbol{\varepsilon}_{\mathbf{k}\sigma} + e^{-i\mathbf{k}\cdot\mathbf{R}}a^\dagger_{\mathbf{k}\sigma}\boldsymbol{\varepsilon}^*_{\mathbf{k}\sigma}\right) \\ \cdot\left(e^{i\mathbf{k}'\cdot\mathbf{R}}a_{\mathbf{k}'\sigma'}\boldsymbol{\varepsilon}_{\mathbf{k}'\sigma'} + e^{-i\mathbf{k}'\cdot\mathbf{R}}a^\dagger_{\mathbf{k}'\sigma'}\boldsymbol{\varepsilon}^*_{\mathbf{k}'\sigma'}\right)\left|\mathbf{q}_I;\mathbf{k}_I,\sigma_I\right\rangle\end{array}\right].$$

This expression is not nearly as fearsome as it appears. The only non-vanishing terms in this double sum occur when we annihilate the correct photon in the initial state, and create the correct photon in the final state. There are exactly two terms in the double sum which survive, and they are effectively identical.

$$\mathcal{T}_{FI} = \frac{e^2}{2m}\frac{\hbar}{\varepsilon_0 V\sqrt{\omega_{k_I}\omega_{k_F}}}\left\langle \mathbf{q}_F;\mathbf{k}_F,\sigma_F \left| e^{-i\mathbf{k}_F\cdot\mathbf{R}}a^\dagger_{\mathbf{k}_F\sigma_F}e^{i\mathbf{k}_I\cdot\mathbf{R}}a_{\mathbf{k}_I\sigma_I}\left(\boldsymbol{\varepsilon}^*_{\mathbf{k}_F\sigma_F}\cdot\boldsymbol{\varepsilon}_{\mathbf{k}_I\sigma_I}\right)\right|\mathbf{q}_I;\mathbf{k}_I,\sigma_I\right\rangle,$$

$$\mathcal{T}_{FI} = \left(\boldsymbol{\varepsilon}^*_F\cdot\boldsymbol{\varepsilon}_I\right)\frac{e^2\hbar}{2m\varepsilon_0 V\sqrt{\omega_I\omega_F}}\left\langle \mathbf{q}_F\left|e^{i\mathbf{k}_I\cdot\mathbf{R}-i\mathbf{k}_F\cdot\mathbf{R}}\right|\mathbf{q}_I\right\rangle. \tag{18.8}$$

This last matrix element is simple to work out:

$$\left\langle \mathbf{q}_F\left|e^{i\mathbf{k}_I\cdot\mathbf{R}-i\mathbf{k}_F\cdot\mathbf{R}}\right|\mathbf{q}_I\right\rangle = \frac{1}{V}\int e^{-i\mathbf{q}_F\cdot\mathbf{r}}e^{i\mathbf{k}_I\cdot\mathbf{r}-i\mathbf{k}_F\cdot\mathbf{r}}e^{i\mathbf{q}_I\cdot\mathbf{r}}d^3\mathbf{r} = \delta_{\mathbf{q}_F+\mathbf{k}_F,\mathbf{q}_I+\mathbf{k}_I}\ .$$

This matrix element does nothing more than ensure conservation of momentum. Substituting it into (18.8) and then into (18.1), and noting that squaring a Kronecker delta function has no effect, we find

$$\mathcal{T}_{FI} = \left(\boldsymbol{\varepsilon}^*_F\cdot\boldsymbol{\varepsilon}_I\right)\frac{e^2\hbar}{2m\varepsilon_0 V\sqrt{\omega_I\omega_F}}\delta_{\mathbf{q}_F+\mathbf{k}_F,\mathbf{q}_I+\mathbf{k}_I}\ , \tag{18.9a}$$

$$\Gamma(I\to F) = \frac{2\pi}{\hbar}\left|\boldsymbol{\varepsilon}^*_F\cdot\boldsymbol{\varepsilon}_I\right|^2\frac{e^4\hbar^2}{4m^2\varepsilon_0^2V^2\omega_I\omega_F}\delta_{\mathbf{q}_F+\mathbf{k}_F,\mathbf{q}_I+\mathbf{k}_I}\delta\left(E_F-E_I\right). \tag{18.9b}$$

Equation (18.9b) is difficult to understand as it stands, because we are still in the infinite volume limit, and because the probabilities of scattering into a *particular* state are small. To make sense of it, sum over all possible final quantum states; that is, sum over the wave numbers for both the electron and the photon, and summing over polarizations of the photon. Let's also put in the explicit form for the energy difference, where the energy is just the energy of the electron plus the photon. We find

$$\Gamma(I\to F) = \sum_{\mathbf{k}_F\sigma_F}\sum_{\mathbf{q}_F}\left|\boldsymbol{\varepsilon}^*_F\cdot\boldsymbol{\varepsilon}_I\right|^2\frac{\pi e^4\hbar}{2m^2\varepsilon_0^2V^2\omega_I\omega_F}\delta_{\mathbf{q}_F+\mathbf{k}_F,\mathbf{q}_I+\mathbf{k}_I}\delta\left(E_F-E_I\right)$$

$$= \sum_{\mathbf{k}_F\sigma_F}\left|\boldsymbol{\varepsilon}^*_F\cdot\boldsymbol{\varepsilon}_I\right|^2\frac{\pi e^4\hbar}{2m^2\varepsilon_0^2V^2\omega_I\omega_F}\delta\left(\hbar\omega_F+\frac{\hbar^2q_F^2}{2m}-\hbar\omega_I\right),$$

$$\Gamma\left(I \to F\right) = \frac{1}{V}\sum_{\sigma_F}\int \frac{d^3\mathbf{k}_F}{\left(2\pi\right)^3}\left|\boldsymbol{\varepsilon}_F^* \cdot \boldsymbol{\varepsilon}_I\right|^2 \frac{\pi e^4\hbar}{2m^2\varepsilon_0^2\omega_I\omega_F}\delta\left(\hbar\omega_F + \frac{\hbar^2 q_F^2}{2m} - \hbar\omega_I\right). \quad (18.10)$$

Now, if the initial wave number is k_I, conservation of momentum will tend to make the final photon and electron wave numbers comparable. We have, therefore,

$$\frac{\hbar^2 q_F^2}{2m} \sim \frac{\hbar^2 k_I^2}{m} \sim \frac{\hbar^2\omega_I^2}{mc^2} = \hbar\omega_I\left(\frac{\hbar\omega_I}{mc^2}\right) \ll \hbar\omega_I \ .$$

Hence in (18.10) we can ignore the electron energy compared to the photon energies, so $\omega_I = \omega_F = \omega$, and we have

$$\begin{aligned}\Gamma\left(I \to F\right) &= \frac{1}{V}\frac{e^4\hbar}{16\pi^2 m^2\varepsilon_0^2\omega^2}\sum_{\sigma_F}\int_0^\infty k_F^2 dk_F \int d\Omega_k \left|\boldsymbol{\varepsilon}_F^* \cdot \boldsymbol{\varepsilon}_I\right|^2 \delta\left(\hbar c k_F - \hbar c k_I\right) \\ &= \frac{1}{V}\frac{e^4 k_F^2}{16\pi^2 m^2\varepsilon_0^2\omega^2 c}\int d\Omega_k \sum_{\sigma_F}\left|\boldsymbol{\varepsilon}_F^* \cdot \boldsymbol{\varepsilon}_I\right|^2 = \frac{1}{V}\frac{\alpha^2\hbar^2}{m^2 c}\int d\Omega_k \sum_{\sigma_F}\left|\boldsymbol{\varepsilon}_F^* \cdot \boldsymbol{\varepsilon}_I\right|^2 ,\end{aligned}$$

where in the last step we wrote our expression in terms of the fine structure constant $\alpha = e^2 / 4\pi\varepsilon_0\hbar c$.

One disturbing fact is that the rate is still inversely proportional to the total volume. This is simply because we are trying to collide a single photon in the universe with a single electron. Under such circumstances, the correct description is not in terms of rates, but in terms of cross section, where the rate is the cross section times the density of targets ($1/V$ in this case) times the relative velocity (c in this case). Hence the cross section is

$$\sigma = \frac{V}{c}\Gamma\left(I \to F\right) = \frac{\alpha^2\hbar^2}{m^2c^2}\int d\Omega_k \sum_{\sigma_F}\left|\boldsymbol{\varepsilon}_F^* \cdot \boldsymbol{\varepsilon}_I\right|^2 = \frac{\alpha^2\hbar^2}{m^2c^2}\int d\Omega_k \sin^2\theta = \frac{8\pi\alpha^2\hbar^2}{3m^2c^2} .$$

If the polarized or unpolarized differential cross-section is desired instead, we can simply not perform the final sums and integral. The angle θ is the angle between the polarization of the incoming wave and the direction of the outgoing wave. This cross-section can be calculated classically, and is called the Thomson cross-section, but it is comforting to find the quantum result agrees with it. With a bit more work, it can be shown that this cross-section is still valid if the initial electron is moving, provided such motion is non-relativistic.

G. Scattering Away From a Resonance

Let us now move to the other extreme. Suppose that instead of a free electron, you have bound electrons in the ground state of the atom, and that the energy of the photon is insufficient to free the electron. We'll also assume we are far from *resonance*, so that the photon energy is not right, nor close to right, to excite the atom to an intermediate state, so that $\varepsilon_I + \hbar\omega_I \neq \varepsilon_m$ for any intermediate state. We will furthermore assume that the final state of the atom is identical to the initial state, so $\omega_I = \omega_F = \omega$ and $|\phi_F\rangle = |\phi_I\rangle$. We need to calculate the matrix elements in eq. (18.7), so we need

$$\mathcal{T}_{FI} = \langle \phi_I; \mathbf{k}_F, \sigma_F | W^{(2)} | \phi_I; \mathbf{k}_I, \sigma_I \rangle + \lim_{\delta\to 0^+} \sum_m \left\{ \frac{\langle \phi_I; \mathbf{k}_F, \sigma_F | W^{(1)} | \phi_m \rangle \langle \phi_m | W^{(1)} | \phi_I; \mathbf{k}_I, \sigma_I \rangle}{\varepsilon_I - \varepsilon_m + \hbar\omega + i\delta} \right.$$
$$\left. + \frac{\langle \phi_I; \mathbf{k}_F, \sigma_F | W^{(1)} | \phi_m; \mathbf{k}_I, \sigma_I; \mathbf{k}_F, \sigma_F \rangle \langle \phi_m; \mathbf{k}_I, \sigma_I; \mathbf{k}_F, \sigma_F | W^{(1)} | \phi_I; \mathbf{k}_I, \sigma_I \rangle}{\varepsilon_I - \varepsilon_m - \hbar\omega + i\delta} \right\}. \quad (18.11)$$

We start with the first term, which in a manner similar to before, yields

$$\mathcal{T}_{FI}(1) = \left(\boldsymbol{\varepsilon}_F^* \cdot \boldsymbol{\varepsilon}_I\right) \frac{e^2\hbar}{2m\varepsilon_0 V\omega} \sum_{j=1}^{N} \langle \phi_I | e^{i\mathbf{k}_I\cdot\mathbf{R}_j - i\mathbf{k}_F\cdot\mathbf{R}_j} | \phi_I \rangle .$$

Now, as we have argued before, the wavelength of light that causes transitions tends to be much larger than the size of an atom, and we are by assumption working at energies of the same order or lower, so we can approximate $e^{i\mathbf{k}_I\cdot\mathbf{R}_j - i\mathbf{k}_F\cdot\mathbf{R}_j} = 1$, and we have

$$\mathcal{T}_{FI}(1) = \left(\boldsymbol{\varepsilon}_F^* \cdot \boldsymbol{\varepsilon}_I\right) \frac{e^2\hbar}{2m\varepsilon_0 V\omega} \sum_{j=1}^{N} \langle \phi_I | \phi_I \rangle = \left(\boldsymbol{\varepsilon}_F^* \cdot \boldsymbol{\varepsilon}_I\right) \frac{e^2\hbar N}{2m\varepsilon_0 V\omega} . \quad (18.12)$$

Now let's look at the second term in (18.11), which, when expanded out a bit, is

$$\mathcal{T}_{FI}(2) = \frac{e^2}{m^2} \lim_{\delta\to 0^+} \sum_m \sum_{j,i=1}^{N} \frac{\langle \phi_I; \mathbf{k}_F, \sigma_F | \left(\mathbf{A}_j \cdot \mathbf{P}_j + \mathbf{B}_j \cdot \mathbf{S}_j\right) | \phi_m \rangle \langle \phi_m | \left(\mathbf{A}_i \cdot \mathbf{P}_i + \mathbf{B}_i \cdot \mathbf{S}_i\right) | \phi_I; \mathbf{k}_I, \sigma_I \rangle}{\varepsilon_I - \varepsilon_m + \hbar\omega + i\delta} .$$

As we have found before, the $\mathbf{A}_j \cdot \mathbf{P}_j$ terms tend to dominate the $\mathbf{B}_j \cdot \mathbf{S}_j$ terms. Furthermore, in the sum over all the photon operators, only the term that annihilates the correct photon and then creates the correct photon contributes. So we find

$$\mathcal{T}_{FI}(2) = \frac{e^2}{m^2} \frac{\hbar}{2\varepsilon_0 V\omega} \lim_{\delta\to 0^+} \sum_m \sum_{j=1}^{N} \sum_{i=1}^{N} \frac{\langle \phi_I | e^{-i\mathbf{k}_F\cdot\mathbf{R}_j} \boldsymbol{\varepsilon}_F^* \cdot \mathbf{P}_j | \phi_m \rangle \langle \phi_m | e^{i\mathbf{k}_I\cdot\mathbf{R}_i} \boldsymbol{\varepsilon}_I \cdot \mathbf{P}_i | \phi_I \rangle}{\varepsilon_I - \varepsilon_m + \hbar\omega + i\delta} .$$

As usual, we then approximate $e^{i\mathbf{k}_I\cdot R_i} = 1 = e^{-i\mathbf{k}_F\cdot\mathbf{R}_j}$, and rewrite the sums as the total momentum. We also replace $\varepsilon_I - \varepsilon_m = -\hbar\omega_{mI}$ to yield

$$\mathcal{T}_{FI}(2) = -\frac{e^2}{2\varepsilon_0 V m^2} \lim_{\delta\to 0^+} \sum_m \frac{\langle \phi_I | \boldsymbol{\varepsilon}_F^* \cdot \mathbf{P} | \phi_m \rangle \langle \phi_m | \boldsymbol{\varepsilon}_I \cdot \mathbf{P} | \phi_I \rangle}{\omega\left(\omega_{mI} - \omega - i\delta\right)} . \quad (18.13)$$

Since we are assuming we are not near resonance, we can take the limit $\delta \to 0$. We rewrite the denominator as

$$\frac{1}{\omega\left(\omega_{mI} - \omega\right)} = \frac{1}{\omega\omega_{mI}} + \frac{1}{\omega_{mI}\left(\omega_{mI} - \omega\right)} .$$

Substituting this into (18.13), we have

$$\mathcal{T}_{FI}(2) = -\frac{e^2}{2\varepsilon_0 V m^2}\sum_m \frac{\langle\phi_I|\boldsymbol{\varepsilon}_F^*\cdot\mathbf{P}|\phi_m\rangle\langle\phi_m|\boldsymbol{\varepsilon}_I\cdot\mathbf{P}|\phi_I\rangle}{\omega_{mI}}\left(\frac{1}{\omega}+\frac{1}{\omega_{mI}-\omega}\right).$$

We now use the same trick we found in equation (15.27), $\langle\phi_m|\mathbf{P}|\phi_I\rangle = im\omega_{mI}\langle\phi_m|\mathbf{R}|\phi_I\rangle$, but for the first term we use this only once, while for the second we use it twice, to yield

$$\mathcal{T}_{FI}(2) = \frac{e^2}{2\varepsilon_0 V}\sum_m \langle\phi_I|\boldsymbol{\varepsilon}_F^*\cdot\mathbf{R}|\phi_m\rangle\left(\frac{i\langle\phi_m|\boldsymbol{\varepsilon}_I\cdot\mathbf{P}|\phi_I\rangle}{m\omega}-\frac{\omega_{mI}\langle\phi_m|\boldsymbol{\varepsilon}_I\cdot\mathbf{R}|\phi_I\rangle}{\omega_{mI}-\omega}\right).$$

In the first term, we now note that we have a complete sum over intermediate states, and no other factors depending on the intermediate state. On the final term we rewrite $\langle\phi_m|\mathbf{R}|\phi_I\rangle = \mathbf{r}_{mI}$ so we can rewrite this term in a nicer form to yield

$$\mathcal{T}_{FI}(2) = \frac{ie^2}{2m\varepsilon_0 V\omega}\langle\phi_I|(\boldsymbol{\varepsilon}_F^*\cdot\mathbf{R})(\boldsymbol{\varepsilon}_I\cdot\mathbf{P})|\phi_I\rangle - \frac{e^2}{2\varepsilon_0 V}\sum_m \frac{\omega_{mI}(\boldsymbol{\varepsilon}_F^*\cdot\mathbf{r}_{mI}^*)(\boldsymbol{\varepsilon}_I\cdot\mathbf{r}_{mI})}{\omega_{mI}-\omega}. \quad (18.14)$$

We have two terms done; we still have one to go. In a manner similar to before, we keep only those terms that create the final state photon, and then annihilate the initial state photon. We again ignore the exponential factors, and combine the momenta to obtain the total momentum. We eventually arrive at an equation analogous to (18.13):

$$\mathcal{T}_{FI}(3) = -\frac{e^2}{2\varepsilon_0 V m^2}\lim_{\delta\to 0^+}\sum_m \frac{\langle\phi_I|\boldsymbol{\varepsilon}_I\cdot\mathbf{P}|\phi_m\rangle\langle\phi_m|\boldsymbol{\varepsilon}_F^*\cdot\mathbf{P}|\phi_I\rangle}{\omega(\omega_{mI}+\omega-i\delta)}.$$

Notice the denominator is slightly different, since in this case we have an *extra* photon in the intermediate state. We again expand out the denominator and then use the same trick we always do for turning momentum matrix elements into position matrix elements, so

$$\begin{aligned}\mathcal{T}_{FI}(3) &= \frac{e^2}{2\varepsilon_0 V}\sum_m\left(\frac{-i\langle\phi_I|\boldsymbol{\varepsilon}_I\cdot\mathbf{P}|\phi_m\rangle}{m\omega}+\frac{\omega_{mI}\langle\phi_I|\boldsymbol{\varepsilon}_I\cdot\mathbf{R}|\phi_m\rangle}{\omega_{mI}+\omega}\right)\langle\phi_m|\boldsymbol{\varepsilon}_F^*\cdot\mathbf{R}|\phi_I\rangle\\ &= \frac{-ie^2}{2m\varepsilon_0 V\omega}\langle\phi_I|(\boldsymbol{\varepsilon}_I\cdot\mathbf{P})(\boldsymbol{\varepsilon}_F^*\cdot\mathbf{R})|\phi_I\rangle + \frac{e^2}{2\varepsilon_0 V}\sum_m\frac{\omega_{mI}(\boldsymbol{\varepsilon}_I\cdot\mathbf{r}_{mI}^*)(\boldsymbol{\varepsilon}_F^*\cdot\mathbf{r}_{mI})}{\omega_{mI}+\omega}. \quad (18.15)\end{aligned}$$

Now that we have the three pieces, all we need to do is put them together. To simplify matters slightly, I'll assume we are working with real polarizations or real dipole moments $\mathbf{r}_{mI}$. Combining (18.12), (18.14), and (18.15), we have

$$\begin{aligned}\mathcal{T}_{FI} &= \mathcal{T}_{FI}(1)+\mathcal{T}_{FI}(2)+\mathcal{T}_{FI}(3)\\ &= \frac{e^2\hbar N}{2m\varepsilon_0 V\omega}(\boldsymbol{\varepsilon}_F^*\cdot\boldsymbol{\varepsilon}_I) + \frac{ie^2}{2m\varepsilon_0 V\omega}\langle\phi_I|\left[(\boldsymbol{\varepsilon}_F^*\cdot\mathbf{R})(\boldsymbol{\varepsilon}_I\cdot\mathbf{P})-(\boldsymbol{\varepsilon}_I\cdot\mathbf{P})(\boldsymbol{\varepsilon}_F^*\cdot\mathbf{R})\right]|\phi_I\rangle\\ &\quad + \frac{e^2}{2\varepsilon_0 V}\sum_m(\boldsymbol{\varepsilon}_F\cdot\mathbf{r}_{mI})^*(\boldsymbol{\varepsilon}_I\cdot\mathbf{r}_{mI})\left(\frac{\omega_{mI}}{\omega_{mI}+\omega}-\frac{\omega_{mI}}{\omega_{mI}-\omega}\right). \quad (18.16)\end{aligned}$$

Now, in the second term, we note that we have a commutator. Keeping in mind that we have several electrons, this commutator can be worked out to yield

$$\left[\boldsymbol{\varepsilon}_F^*\cdot\mathbf{R},\boldsymbol{\varepsilon}_I\cdot\mathbf{P}\right]=\sum_{j=1}^N\sum_{i=1}^N\left[\boldsymbol{\varepsilon}_F^*\cdot\mathbf{R}_j,\boldsymbol{\varepsilon}_I\cdot\mathbf{P}_i\right]=\sum_{j=1}^N\sum_{i=1}^N i\hbar\delta_{ji}\left(\boldsymbol{\varepsilon}_F^*\cdot\boldsymbol{\varepsilon}_I\right)=Ni\hbar\left(\boldsymbol{\varepsilon}_F^*\cdot\boldsymbol{\varepsilon}_I\right).$$

Substituting this into (18.16), we find the first two terms cancel exactly, so we have

$$\mathcal{T}_{FI}=-\frac{e^2}{\varepsilon_0 V}\sum_m\frac{\omega\omega_{mI}}{\omega_{mI}^2-\omega^2}\left(\boldsymbol{\varepsilon}_F\cdot\mathbf{r}_{mI}\right)^*\left(\boldsymbol{\varepsilon}_I\cdot\mathbf{r}_{mI}\right). \tag{18.17}$$

We can then substitute this into (18.1) to obtain a rate per unit volume, which in turn can be converted into a cross-section.

Let us compare the size of the amplitude (18.17) we found for a bound electron to that for a free electron, (18.9a). Ignoring matching factors, and making only order of magnitude estimates, we find

$$\frac{\mathcal{T}_{FI}\left(\text{bound}\right)}{\mathcal{T}_{FI}\left(\text{free}\right)}\sim\frac{m\omega^2\omega_{mI}\left|\mathbf{r}_{mI}\right|^2}{\hbar\left(\omega_{mI}^2-\omega^2\right)}.$$

For a typical atom, we would expect $\omega_{mI}\sim mc^2\alpha^2/\hbar$ and $\left|\mathbf{r}_{mI}\right|\sim\left(\hbar/\alpha mc\right)$, so we have

$$\frac{\mathcal{T}_{FI}\left(\text{bound}\right)}{\mathcal{T}_{FI}\left(\text{free}\right)}\sim\frac{\omega^2}{\omega_{mI}^2-\omega^2}.$$

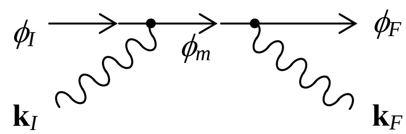
Suppose that we have *tightly* bound atom, so that $\omega/\omega_{mI}\ll 1$. Then this ratio is of order $\left(\omega/\omega_{mI}\right)^2$, and this gets squared to $\left(\omega/\omega_{mI}\right)^4$ when you calculate the rate (which ultimately becomes a cross-section). Hence a tightly bound atom has a much lower cross-section than a free electron for photon scattering.

This has considerable significance in the early universe. The early universe was at very high temperatures, hot enough that electrons were not generally bound into atoms, but rather free. This meant that the early universe was opaque, and photons effectively were in near perfect equilibrium. However, when the temperature of the universe dropped to about 3000 K, at an age of about 380,000 years, the electrons became bound to the free protons to produce neutral hydrogen atoms. Since the typical photon had an energy of about $3k_BT\approx 0.8\text{ eV}$, and the first excited state of hydrogen requires about 10.2 eV of energy, the cross-section dropped suddenly by several orders of magnitude, and the universe became transparent. These photons have since been red-shifted in the expanding universe, and now appear as a nearly uniform 2.73 K background. This background gives us a snapshot of what the universe looked like at t = 380,000 y.

Our derivation of (18.17) assumed that we were working away from resonance. However, as $\omega\to\omega_{mI}$, it is clear from (18.17) that something dramatic may occur, since there will be a sudden increase in the amplitude. Under such *resonance* conditions, we need to rethink how we are computing our amplitude. This complication is the subject of the next section.

It should be understood that, as usual, we have included only the dipole approximation in our scattering amplitude. This is generally a good approximation, since we are summing over all intermediate states, and those which have non-zero dipole moment will tend to dominate. But if we approach resonance, so $\omega \approx \omega_{mI}$ for some state that does *not* have a dipole moment, we will have to include "smaller" effects like the electric quadrupole or magnetic dipole. These small matrix elements will be greatly enhanced by the nearly vanishing denominators.

H. Scattering Near a Resonance

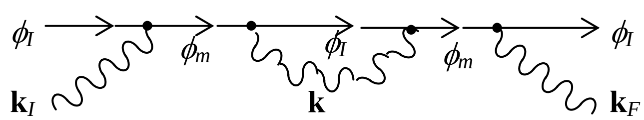


It is evident from equation (18.17) that our amplitudes may become large when $\omega \approx \omega_{mI}$. The large amplitude can be traced back to the contribution from $\mathcal{T}_{FI}(2)$, corresponding to the diagram sketched above. It is easy to see why this term dominates: the intermediate state has almost exactly the right energy to match the incoming energy. Indeed, we will focus exclusively on this diagram, and only include one term in the sum, the one which has a small energy denominator. The amplitude for this is given by (18.14), repeated here, but with the standard substitution $\langle \phi_m | \mathbf{P} | \phi_I \rangle = im\omega_{mI}\mathbf{r}_{mI}$

$$\mathcal{T}_{FI}^{(0)} = \frac{e^2\omega_{mI}^2}{2\varepsilon_0 V\omega} \lim_{\delta\to 0^+} \frac{\left(\boldsymbol{\varepsilon}_F^* \cdot \mathbf{r}_{mI}^*\right)\left(\boldsymbol{\varepsilon}_I \cdot \mathbf{r}_{mI}\right)}{\omega - \omega_{mI} + i\delta}. \tag{18.18}$$

My notation has changed slightly; I have dropped the (2), because when we are close to resonance, this will effectively be the *only* term we need to worry about, and the (0) is because in a moment we will be adding higher and higher order terms to try to figure out what is going on. This diagram has zero loops in it.

If we were to continue with this expression, we would ultimately obtain a cross section that diverges at $\omega = \omega_{mI}$. What is the solution to this problem? The answer turns out, somewhat surprisingly, to add more diagrams. Consider now the one-loop diagram sketched at right. In this diagram, the ground state atom merges with a photon to produce the resonant excited state, then it splits into an intermediate photon of wave number $\mathbf{k}$ and the ground state again, which then remerges to produce the excited state before splitting back into a photon and the ground state.



Fortunately, nearly all the work has already been done, and we simply reuse it. The two new vertices (in the middle) are virtually identical to the ones we had before, and we now have two intermediate states that are purely the resonant state. The main new feature is an energy denominator, which looks like $\varepsilon_I + \hbar\omega - \varepsilon_I - \hbar\omega_{\mathbf{k}} + i\delta$, so we have

$$\mathcal{T}_{FI}^{(1)}(\mathbf{k},\sigma) = \left(\frac{e^2\omega_{mI}^2}{2\varepsilon_0 V\omega}\right)^2 \lim_{\delta\to 0^+} \frac{\left(\boldsymbol{\varepsilon}_F^* \cdot \mathbf{r}_{mI}^*\right)\left(\boldsymbol{\varepsilon}_{\mathbf{k}\sigma} \cdot \mathbf{r}_{mI}\right)\left(\boldsymbol{\varepsilon}_{\mathbf{k}\sigma}^* \cdot \mathbf{r}_{mI}^*\right)\left(\boldsymbol{\varepsilon}_I \cdot \mathbf{r}_{mI}\right)}{\left(\omega - \omega_{mI} + i\delta\right)^2\left(\hbar\omega - \hbar\omega_{\mathbf{k}} + i\delta\right)},$$

$$\mathcal{T}_{FI}^{(1)}(\mathbf{k},\sigma) = \mathcal{T}_{FI}^{(0)}\left(\frac{e^2\omega_{mI}^2}{2\varepsilon_0 V\omega}\right)\frac{(\boldsymbol{\varepsilon}_{\mathbf{k}\sigma}\cdot\mathbf{r}_{mI})(\boldsymbol{\varepsilon}_{\mathbf{k}\sigma}^*\cdot\mathbf{r}_{mI}^*)}{(\omega-\omega_{mI}+i\delta)(\hbar\omega-\hbar\omega_{\mathbf{k}}+i\delta)}.$$

This is the amplitude from this diagram for a *particular* intermediate momentum and polarization. Of course, we don't measure this intermediate state, so we must actually sum over all such intermediate states. We then turn the sum into an integral in the infinite volume limit in the usual way, and have

$$\mathcal{T}_{FI}^{(1)} = \mathcal{T}_{FI}^{(0)}\frac{1}{\omega-\omega_{mI}+i\delta}\frac{e^2\omega_{mI}^2}{2\varepsilon_0\omega\hbar}\sum_\sigma\int\frac{d^3\mathbf{k}}{(2\pi)^3}\frac{\left|\boldsymbol{\varepsilon}_{\mathbf{k}\sigma}\cdot\mathbf{r}_{mI}\right|^2}{\omega-\omega_{\mathbf{k}}+i\delta}. \tag{18.19}$$

Note that there is an implied $\lim_{\delta\to 0^+}$ in $\mathcal{T}_{FI}^{(0)}$, which applies to every factor in (18.19).

Now, we will be interested in the integral appearing in (18.19). We will split it into a real and imaginary part, which we write as

$$\Delta(\omega)-\tfrac{1}{2}i\Gamma(\omega) \equiv \frac{e^2\omega_{mI}^2}{2\varepsilon_0\omega\hbar}\sum_\sigma\int\frac{d^3\mathbf{k}}{(2\pi)^3}\frac{\left|\boldsymbol{\varepsilon}_{\mathbf{k}\sigma}\cdot\mathbf{r}_{mI}\right|^2}{\omega-\omega_{\mathbf{k}}+i\delta}, \tag{18.20}$$

where $\Delta(\omega)$ and $\Gamma(\omega)$ are real functions of ω. Switching to spherical coordinates, and remembering that $k=\omega_k/c$, and substituting the fine structure constant $\alpha = e^2/4\pi\varepsilon_0\hbar c$, we have

$$\Delta(\omega)-\tfrac{1}{2}i\Gamma(\omega) = \sum_\sigma\int d\Omega_{\mathbf{k}}\int_0^\infty \omega_k^2 d\omega_k\frac{\alpha\omega_{mI}^2\left|\boldsymbol{\varepsilon}_{\mathbf{k}\sigma}\cdot\mathbf{r}_{mI}\right|^2}{4\pi^2c^2\omega(\omega-\omega_k+i\delta)}. \tag{18.21}$$

At the moment, I am not particularly interested in the real part. Indeed, if you continue the computation, you will discover that it is divergent, but this divergence is only present because we approximate the phase factors as $e^{i\mathbf{k}\cdot\mathbf{R}_j}=1$ in all our matrix elements. The infinity is coming from the high frequency modes, when this approximation breaks down, and one would ultimately find some finite contribution to $\Delta(\omega)$. In the limit $\delta\to 0^+$, the integral is zero almost everywhere, except for a small region right around $\omega_k=\omega$. We can therefore concentrate on this small region to find the imaginary part. Let us take the limit $\delta\to 0^+$, but let's distort the path of integration in this region so that we avoid the divergence. The $i\delta$ tells us how to do this: We want to keep the combination $\omega-\omega_k+i\delta$ positive imaginary, which we do by letting ω_k have a small negative imaginary part, as illustrated in Fig. 18-3. We can now let $\delta=0$ in the denominator, but for the little hop below the real axis, we let $\omega_k=\omega-\delta e^{i\theta}$. Thus as θ progresses from 0 to π, the little half-loop will be followed. We will treat δ as so small that effectively it equals zero, except in the critical denominator. Focusing on the

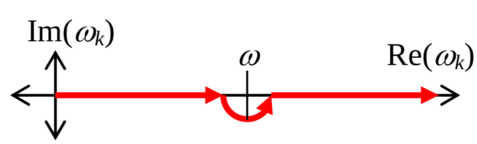


Figure 18-3: The path for integration for Eq. (18.21). The only part that contributes to the imaginary part is the little "hop" below that real axis near $\omega_k=\omega$.

imaginary part, we substitute $\omega_k = \omega - \delta e^{i\theta}$ into (18.21), and find

$$\begin{aligned}
\Gamma(\omega) &= -2\,\mathrm{Im}\left\{ \sum_\sigma \int d\Omega_{\mathbf{k}} \int_0^\pi \left(\omega - \delta e^{i\theta}\right)^2 d\left(\omega - \delta e^{i\theta}\right) \frac{\alpha\omega_{mI}^2 \left|\boldsymbol{\varepsilon}_{\mathbf{k}\sigma} \cdot \mathbf{r}_{mI}\right|^2}{4\pi^2 c^2 \omega \left(\omega - \omega + \delta e^{i\theta}\right)} \right\} \\
&= 2\,\mathrm{Im}\left\{ \sum_\sigma \int d\Omega_{\mathbf{k}} \frac{\omega^2 \alpha\omega_{mI}^2 \left|\boldsymbol{\varepsilon}_{\mathbf{k}\sigma} \cdot \mathbf{r}_{mI}\right|^2}{4\pi^2 c^2 \omega} \int_0^\pi \frac{i\delta e^{i\theta} d\theta}{\delta e^{i\theta}} \right\} = \frac{\alpha\omega_{mI}^2 \omega}{2\pi c^2} \sum_\sigma \int d\Omega_{\mathbf{k}} \left|\boldsymbol{\varepsilon}_{\mathbf{k}\sigma} \cdot \mathbf{r}_{mI}\right|^2 \\
&= \frac{\alpha\omega_{mI}^2 \omega \left|\mathbf{r}_{mI}\right|^2}{2\pi c^2} \int \sin^2\theta_{\mathbf{k}} d\Omega_{\mathbf{k}} = \frac{4\alpha\omega_{mI}^2 \omega \left|\mathbf{r}_{mI}\right|^2}{3c^2}. \qquad (18.22)
\end{aligned}$$

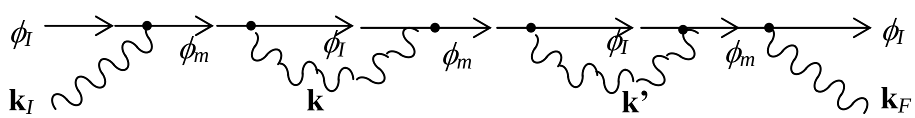
Compare the result (18.22) with eq. (18.5). It is virtually identical. It is something like a frequency dependant decay rate for the intermediate state $\left|\phi_m\right\rangle$. Indeed, if we are working near resonance, then they *are* identical.

Substituting (18.20) into (18.19) will then yield

$$\mathcal{T}_{FI}^{(1)} = \mathcal{T}_{FI}^{(0)} \frac{\Delta(\omega) - \frac{1}{2} i\Gamma(\omega)}{\omega - \omega_{mI} + i\delta}. \qquad (18.23)$$

We don't know what $\Delta(\omega)$ exactly is, but we won't need it in the subsequent discussion, but we *do* know the explicit form of $\Gamma(\omega)$. However, all we need to know for now is that they are both finite.

Now, as we look at (18.23), it seems that our situation is worse than ever. Recall that our original amplitude $\mathcal{T}_{FI}^{(0)}$ given by (18.18) diverges at resonance. The new term (18.23) has yet another denominator, and diverges even worse. Let's try adding two loops and see what we get, as sketched at right. This time we can write down the answer instantly: The effect of adding another loop is simply to put yet another factor similar to the one in (18.23). The amplitude, we immediately see, is given by



$$\mathcal{T}_{FI}^{(2)} = \mathcal{T}_{FI}^{(0)} \left[\frac{\Delta(\omega) - \frac{1}{2} i\Gamma(\omega)}{\omega - \omega_{mI} + i\delta} \right]^2.$$

Now that we've established the pattern, we can continue indefinitely. We are most interested in the sum of all these diagrams, which looks like

$$\mathcal{T}_{FI} = \mathcal{T}_{FI}^{(0)} + \mathcal{T}_{FI}^{(1)} + \mathcal{T}_{FI}^{(2)} + \cdots = \mathcal{T}_{FI}^{(0)} \left\{ 1 + \frac{\Delta(\omega) - \frac{1}{2} i\Gamma(\omega)}{\omega - \omega_{mI} + i\delta} + \left[\frac{\Delta(\omega) - \frac{1}{2} i\Gamma(\omega)}{\omega - \omega_{mI} + i\delta} \right]^2 + \cdots \right\}.$$

This is nothing more than a geometric series. Summing it and substituting our explicit form (18.18) for $\mathcal{T}_{FI}^{(0)}$, we have

$$\mathcal{T}_{FI} = \mathcal{T}_{FI}^{(0)} \sum_{n=0}^{\infty} \left[\frac{\Delta(\omega) - \frac{1}{2} i\Gamma(\omega)}{\omega - \omega_{mI} + i\delta} \right]^n = \mathcal{T}_{FI}^{(0)} \left[1 - \frac{\Delta(\omega) - \frac{1}{2} i\Gamma(\omega)}{\omega - \omega_{mI} + i\delta} \right]^{-1}$$

$$= \frac{e^2 \omega_{mI}^2}{2\varepsilon_0 V \omega} \lim_{\delta \to 0^+} \frac{\left(\boldsymbol{\varepsilon}_F^* \cdot \mathbf{r}_{mI}^* \right)\left(\boldsymbol{\varepsilon}_I \cdot \mathbf{r}_{mI} \right)}{\omega - \omega_{mI} + i\delta} \frac{\omega - \omega_{mI} + i\delta}{\omega - \omega_{mI} + i\delta - \left[\Delta(\omega) - \frac{1}{2} i\Gamma(\omega) \right]}$$

$$= \frac{e^2 \omega_{mI}^2}{2\varepsilon_0 V \omega} \lim_{\delta \to 0^+} \frac{\left(\boldsymbol{\varepsilon}_F^* \cdot \mathbf{r}_{mI}^* \right)\left(\boldsymbol{\varepsilon}_I \cdot \mathbf{r}_{mI} \right)}{\omega - \omega_{mI} - \Delta(\omega) + \frac{1}{2} i\Gamma(\omega) + i\delta} . \qquad (18.24)$$

Now, as if by miracle, we note that we can take the limit $\delta \to 0^+$ with impunity. The decay rate $\Gamma(\omega)$ makes the denominator finite. We also now understand the meaning of $\Delta(\omega)$: it is a shift of the intermediate energy for the state $\left|\phi_m\right\rangle$.

We would like to go ahead and calculate the scattering cross-section from (18.24). Substituting into (18.1), we have

$$\Gamma(I \to F) = \frac{2\pi}{\hbar} \left(\frac{e^2 \omega_{mI}^2}{2\varepsilon_0 V \omega} \right)^2 \frac{\left| \boldsymbol{\varepsilon}_F \cdot \mathbf{r}_{mI} \right|^2 \left| \boldsymbol{\varepsilon}_I \cdot \mathbf{r}_{mI} \right|^2}{\left[\omega - \omega_{mI} - \Delta(\omega) \right]^2 + \frac{1}{4} \Gamma^2(\omega)} \delta(E_F - E_I).$$

Let's assume we're working near resonance. We'll neglect the small shift in the energy $\Delta(\omega)$. We also want to sum over final state polarizations and outgoing final state directions. Then we have

$$\Gamma(I \to F) = \frac{2\pi}{\hbar} \frac{e^4 \omega_{mI}^4}{4\varepsilon_0^2 V^2 \omega^2} \sum_{\mathbf{k},\sigma} \frac{\left| \boldsymbol{\varepsilon}_F \cdot \mathbf{r}_{mI} \right|^2 \left| \boldsymbol{\varepsilon}_I \cdot \mathbf{r}_{mI} \right|^2}{\left(\omega - \omega_{mI} \right)^2 + \frac{1}{4} \Gamma^2(\omega)} \delta(E_F - E_I)$$

$$= \frac{\pi e^4 \omega_{mI}^4 \left| \boldsymbol{\varepsilon}_I \cdot \mathbf{r}_{mI} \right|^2}{2\hbar \varepsilon_0^2 V \omega^2} \sum_{\sigma} \int \frac{d^3\mathbf{k}}{(2\pi)^3} \frac{\left| \boldsymbol{\varepsilon}_F \cdot \mathbf{r}_{mI} \right|^2}{\left(\omega - \omega_{mI} \right)^2 + \frac{1}{4} \Gamma^2(\omega)} \delta(E_F - E_I)$$

$$= \frac{e^4 \omega_{mI}^4 \left| \boldsymbol{\varepsilon}_I \cdot \mathbf{r}_{mI} \right|^2}{16\pi^2 \hbar \varepsilon_0^2 V \omega^2} \sum_{\sigma} \int_0^{\infty} \frac{\omega_F^2 d\omega_F}{c^3} \int d\Omega_k \frac{\left| \boldsymbol{\varepsilon}_F \cdot \mathbf{r}_{mI} \right|^2}{\left(\omega - \omega_{mI} \right)^2 + \frac{1}{4} \Gamma^2(\omega)} \delta(\hbar\omega_F - \hbar\omega)$$

$$= \frac{\alpha^2 \omega_{mI}^4 \left| \boldsymbol{\varepsilon}_I \cdot \mathbf{r}_{mI} \right|^2}{Vc\left[\left(\omega - \omega_{mI} \right)^2 + \frac{1}{4} \Gamma^2(\omega) \right]} \sum_{\sigma} \int d\Omega_k \left| \boldsymbol{\varepsilon}_F \cdot \mathbf{r}_{mI} \right|^2 = \frac{8\pi\alpha^2 \omega_{mI}^4 \left| \boldsymbol{\varepsilon}_I \cdot \mathbf{r}_{mI} \right|^2 \left| \mathbf{r}_{mI} \right|^2}{3Vc\left[\left(\omega - \omega_{mI} \right)^2 + \frac{1}{4} \Gamma^2(\omega) \right]}.$$

Because decay rates tend to be rather small, the denominator will have a dramatic increase right at resonance. Note that the rate is still dependant on V, which is hardly surprising, since we are trying to collide one photon with one atom. We need to convert this to a cross section, which we do in the usual way by using the formula $\Gamma = n\sigma\left|\Delta\mathbf{v}\right|$, where $n = 1/V$ is the density of target atoms, and $\left|\Delta\mathbf{v}\right| = c$ is the relative velocity. We find

$$\sigma(\omega) = \frac{8\pi\alpha^2 \omega_{mI}^4 \left| \mathbf{r}_{mI} \right|^2 \left| \boldsymbol{\varepsilon}_I \cdot \mathbf{r}_{mI} \right|^2}{3c^2\left[\left(\omega - \omega_{mI} \right)^2 + \frac{1}{4} \Gamma^2(\omega) \right]}.$$

If we treat $\Gamma(\omega)$ as a constant, this shape is called a *Lorentzian line shape*.

Now, in all our computations, we have been assuming there is only one possible intermediate state, and sometimes this is the case. More typically, however, there will be several degenerate intermediate states, related to each other by rotational symmetry. Normally we can choose one of them to be the state with the dipole moment in the direction of the polarization of the incoming light, so that $|\boldsymbol{\varepsilon}_I \cdot \mathbf{r}_{mI}| = |\mathbf{r}_{mI}|$, and the others will be perpendicular to the dipole moment, and we have

$$\sigma(\omega) = \frac{8\pi\alpha^2\omega_{mI}^4 |\mathbf{r}_{mI}|^4}{3c^2\left[(\omega-\omega_{mI})^2 + \frac{1}{4}\Gamma^2(\omega)\right]}. \tag{18.25}$$

If we perform the scattering right on resonance, at $\omega = \omega_{mI}$, and use our explicit form (18.22) for the rate, we have

$$\sigma(\omega_{mI}) = \frac{8\pi\alpha^2\omega_{mI}^4 |\mathbf{r}_{mI}|^4}{3c^2\,\frac{1}{4}\left[\frac{4}{3}\alpha\omega_{mI}^3 |\mathbf{r}_{mI}|^2 / c^2\right]^2} = \frac{3\pi c^2}{2\omega_{mI}^2}. \tag{18.26}$$

Notice that all the factors of the coupling, matrix elements, and so on, have disappeared.

We have simplified the discussion by assuming that the state $|\phi_m\rangle$ can only decay to the state $|\phi_I\rangle$. When this assumption is false, there will be an additional factor representing essentially the fraction of the time that $|\phi_m\rangle$ decays to $|\phi_I\rangle$. Nonetheless, the cross-section (18.26) is *enormous*; it is of the order of the wavelength squared, which will be tens of thousands of times greater than scattering off of a free electron. This is the power of resonant scattering.

One way to think of this process is that the atom is actually absorbing the photon, staying in an excited state for a brief time, and then re-emitting the photon. Over what range of energies will this absorption occur? We can see from (18.25) that the cross section will be of order its maximum value if $|\omega-\omega_{mI}| < \frac{1}{2}\Gamma$. This means that the energy is "wrong" by an approximate quantity $\Delta E \sim \frac{1}{2}\hbar\Gamma$. The atom will "hang onto" the energy of the photon for a typical time $\Delta t = \Gamma^{-1}$. Multiplying these two quantities yields the time-energy uncertainty relationship, $\Delta E \Delta t \sim \frac{1}{2}\hbar$.

Problems for Chapter 18

1. An electron is trapped in a 3D harmonic oscillator potential, $H = \mathbf{P}^2/2m + \frac{1}{2}m\omega^2\mathbf{R}^2$. It is in the quantum state $\left|n_x, n_y, n_z\right\rangle = \left|2,1,0\right\rangle$
   (a) Calculate every non-vanishing matrix element of the form $\left\langle n_x', n_y', n_z'\right|\mathbf{R}\left|2,1,0\right\rangle$ where the final state is lower in energy than the initial state.
   (b) Calculate the decay rate $\Gamma\left(210 \to n_x', n_y', n_z'\right)$ for this decay in the dipole approximation for every possible final state.

2. A hydrogen atom is initially in a 3d state, specifically, $\left|n, l, m\right\rangle = \left|3, 2, +2\right\rangle$.
   (a) Find all non-zero matrix elements of the form $\left\langle n', l', m'\right|\mathbf{R}\left|3, 2, +2\right\rangle$, where $n' < n$. Which state(s) will it decay into?
   (b) Calculate the decay rate in s^{-1}.

3. An electron is trapped in a 3D harmonic oscillator potential, $H = \mathbf{P}^2/2m + \frac{1}{2}m\omega^2\mathbf{R}^2$. It is in the quantum state $\left|n_x, n_y, n_z\right\rangle = \left|0,0,2\right\rangle$. It is going to decay *directly* into the ground state $\left|0,0,0\right\rangle$
   (a) Convince yourself that it cannot go there via the electric dipole transition. It can, however, go there via the electric quadrupole transition.
   (b) Calculate every non-vanishing matrix element of the form $\left\langle 0,0,0\right|R_i R_j\left|0,0,2\right\rangle$.
   (b) Calculate the polarized differential decay rate $d\Gamma_{\text{pol}}\left(002 \to 000\right)/d\Omega$ for this decay. This will require, among many other things, converting a sum to an integral in the infinite volume limit.
   (c) Sum it over polarizations and integrate it over angles to determine the total decay rate $\Gamma\left(002 \to 000\right)$.

4. The present day density of electrons is about $0.21/\text{m}^3$; however, these electrons are not all free.
   (a) Calculate the cross-section for free photon-electron scattering in m^2. If all the electrons *were* free, what would be the rate at which they scatter, today? How many scatterings would have occurred to an average photon in the age of the universe, 13.7 Gyr?
   (b) The last time the electrons *were* free was when the universe was 1092 times smaller in all three directions, and it was only 380,000 years old. The number of electrons was about the same then (though the number *density* was much higher, since the universe was smaller). Redo part (a) at this time.

5. An electron is trapped in a 3D harmonic oscillator potential, $H = \mathbf{P}^2/2m + \frac{1}{2}m\omega^2\mathbf{R}^2$. It is in the ground state $\left|n_x, n_y, n_z\right\rangle = \left|0,0,0\right\rangle$. Photons are fired at the electron with frequency $\omega \ll \omega_0$, going in the *z*-direction, and polarized in the *x*-direction, $\boldsymbol{\varepsilon} = \hat{\mathbf{x}}$. Calculate the differential cross section $d\sigma/d\Omega$ (summed over final polarizations, not integrated), and the total cross section σ.

6. A Hydrogen atom in the 1s-state is hit by photons polarized in the z-direction very close to $\frac{3}{4}\omega_{\text{Ryd}}$; that is, quite close to the 2p-resonance, where $\omega_{\text{Ryd}} = \alpha^2 mc^2/2\hbar$ is the binding frequency of the ground state of Hydrogen.
   (a) Find all non-zero components of the matrix elements $\langle 210|\mathbf{R}|100\rangle$. Find the decay rate $\Gamma(\omega)$ for this state. $\Gamma(\omega)$ should be proportional to ω; it should be ω times a pure number.
   (b) Calculate a formula for the cross-section as a function of ω. Assume that only one diagram (the one calculated in class) is relevant, the one that has a resonance at the 2p state. Treat the energy shift $\Delta(\omega)$ as zero.
   (c) Sketch the cross-section in units of a_0^2 as a function of ω in the range 0.74 – 0.76 ω_{Ryd}. I recommend making the vertical scale logarithmic.