8

Radiation–matter interactions

The interaction of radiation and matter is a problem, or rather a set of problems, in quantum physics. This is because the spatial scale of the atoms and the typical momenta of the atomic electrons exactly obey the uncertainty limit, $\Delta x \Delta p \gtrsim \hbar$. If this were not true, then the atoms could shrink and find a state of lower energy. Therefore all the atomic properties needed for radiative transfer come from the application of quantum mechanics to the atoms. The quantum mechanical theory presented below is based mostly on Messiah (1962), volume 2. The angular algebra leading to the final results in terms of reduced matrix elements draws on Sobel'man (1979) and Condon and Shortley (1951).

8.1 QED for dummies

The one-paragraph sketch of the quantum mechanics of radiation processes is this: the non-relativistic Hamiltonian of the system comprising an atom and a radiation field is

$$H = -\sum_i \frac{Ze^2}{r_i} + \sum_{i<j} \frac{e^2}{r_{ij}} + \sum_i \frac{1}{2m} \left[\mathbf{p}_i - \frac{e}{c}\mathbf{A}(\mathbf{r}_i) \right]^2$$
$$+ \int dV \frac{1}{8\pi} \left(\mathcal{E}^2 + \mathcal{H}^2 \right), \tag{8.1}$$

where the index i labels the individual atomic electrons, $\mathbf{p}_i$ is the momentum of the ith electron, and $\mathbf{r}_i$ is its position. The vector function $\mathbf{A}(\mathbf{r})$ is the vector potential for the electromagnetic field (in the radiation gauge), and $\mathcal{E}$ and $\mathcal{H}$ are the fields. The electromagnetic field is quantized by expressing $\mathbf{A}$ in terms of the creation and annihilation operators for quanta of the plane-wave basis

states,

$$\mathbf{A}(\mathbf{r}) = \sum_{\mathbf{k}\varpi} \left(\frac{2\pi\hbar c^2}{\omega V}\right)^{1/2} \mathbf{e}_{\mathbf{k}\varpi} \left[a_{\mathbf{k}\varpi}^{\dagger} \exp(-i\mathbf{k}\cdot\mathbf{r}) + a_{\mathbf{k}\varpi} \exp(i\mathbf{k}\cdot\mathbf{r})\right], \quad (8.2)$$

where $a^{\dagger}$ is the creation operator and a is annihilation operator. The wavevectors $\mathbf{k}$ belong to a discrete set corresponding to the modes in a large but finite volume V with periodic boundary conditions. The vectors $\mathbf{e}_{\mathbf{k}\varpi}$, for $\varpi = 1, 2$, are the two electric field polarization directions perpendicular to $\mathbf{k}$, and $\omega = kc$ is the angular frequency associated with $\mathbf{k}$. The interaction terms between radiation and matter are those involving $\mathbf{A}$ that result when the squared terms in (8.1) are expanded, in other words

$$H_{\text{int}} = -\frac{e}{mc} \sum_i \mathbf{p}_i \cdot \mathbf{A}(\mathbf{r}_i) + \frac{e^2}{2mc^2} \sum_i \mathbf{A}(\mathbf{r}_i)^2. \quad (8.3)$$

The transition rates, and therefore cross sections, for various radiative processes are found by treating H_{int} using perturbation theory, which entails finding the matrix element of H_{int} between an initial state $|a\mathbf{n}\rangle$ and a final state $|b\mathbf{n}'\rangle$. Here a and b are labels of atomic states, and the initial state of the radiation field is specified by a vector $\mathbf{n}$ giving the number of photons present in each basis state, and similarly for the final radiation state. The first term in H_{int} is linear in $\mathbf{A}$, therefore this term can allow exactly one photon to be created or alternatively, to be destroyed. The second term is quadratic, therefore this term allows processes that create two photons, destroy two photons, or destroy one and create another. In other words, absorption and emission come from the $\mathbf{p}\cdot\mathbf{A}$ term, and scattering comes from the $\mathbf{A}^2$ term (and also from $\mathbf{p}\cdot\mathbf{A}$ in second order perturbation theory, as it turns out).

The part of the radiation field belonging to one particular basis state, i.e., to one wave vector $\mathbf{k}$ and polarization $\mathbf{e}_{\mathbf{k}\varpi}$, is exactly like a harmonic oscillator. The states are labeled by the occupation number $n_{\mathbf{k}\varpi}$, which takes on the values $0, 1, \ldots$. The occupation number is the eigenvalue of the operator $n_{\mathbf{k}\varpi} = a_{\mathbf{k}\varpi}^{\dagger} a_{\mathbf{k}\varpi}$. The energy of the state is $(n_{\mathbf{k}\varpi} + 1/2)\hbar\omega$, where ω is the angular frequency for this $\mathbf{k}$. When the matrix elements of the interaction are calculated, we end up with something proportional to $\langle n+1|a^{\dagger}|n\rangle$ for a process that produces emission, $\langle n-1|a|n\rangle$ for a process that represents absorption, and a product of matrix elements $\langle n_2+1|a_2^{\dagger}|n_2\rangle\langle n_1-1|a_1|n_1\rangle$ for a scattering process in which a type-1 photon goes away and a type-2 photon is created. All these matrix elements come from the standard harmonic oscillator theory, where $a^{\dagger}$ and a are the raising and lowering

operators. The matrix elements are simple:

$$\langle n + 1|a^\dagger|n\rangle = \sqrt{n+1}, \tag{8.4}$$

$$\langle n - 1|a|n\rangle = \langle n|a^\dagger|n - 1\rangle = \sqrt{n}. \tag{8.5}$$

When we recall that transition rates in first order perturbation theory are proportional to the matrix element of the interaction squared, we see that emission rates are proportional to 1 plus the number of photons initially present; absorption rates are proportional to the number of photons initially present. What is the implication for scattering? We square the product of the two matrix elements and find something proportional to $n_1(n_2 + 1)$, i.e., proportional to the number of photons in the out-scattering state, and 1 plus the number of photons in the in-scattering state. The reverse scattering process, in which a type-2 photon goes away and a type-1 photon is created has a rate proportional to $n_2(n_1 + 1)$. You might think that the $n_1 n_2$ part of these rates just cancels out, and this is almost true. There is a correction because the frequencies of the photons are not exactly equal, as we will discuss later in connection with the Kompaneets equation.

8.2 Emission and absorption; Einstein coefficients

We consider the emission of a photon by an atom in an excited state b as it makes a transition to a lower state a. The transition probability per unit time is given by Fermi's Golden Rule as

$$w_{ba} = \frac{2\pi}{\hbar}|\langle a, n + 1|H_{\text{int}}|b, n\rangle|^2\rho(E), \tag{8.6}$$

where $\rho(E)$ is the number of photon basis states per unit energy near $E = \hbar\omega = E_a - E_b$, the amount of energy lost by the atom; the volume V has been assumed so large that the photon states form a pseudo-continuum. The occupation number n of the states has been assumed to be smooth around this energy. The steps we take next to reduce (8.6) are to: substitute the $a^\dagger$ term from the expansion of $\mathbf{p} \cdot \mathbf{A}$ for H_{int}; impose the dipole approximation which is obtained on setting $\exp(i\mathbf{k} \cdot \mathbf{r}) \approx 1$ and is valid when $kr \ll 1$, i.e., when the radiation wavelength is much larger than the atom; substitute

$$\rho(E) = \frac{V k^2\, dk\, d\Omega}{(2\pi)^3\hbar c\, dk} = \frac{V k^2}{8\pi^3\hbar c}d\Omega; \tag{8.7}$$

sum the results over the two possible polarizations of the emitted photon; and integrate the answer over all directions of emission. One tricky bit is this step:

$$\int_{4\pi}\sum_{\varpi}\langle a|\mathbf{p}|b\rangle^* \cdot \mathbf{e}_{\mathbf{k}\varpi}\mathbf{e}_{\mathbf{k}\varpi} \cdot \langle a|\mathbf{p}|b\rangle = \frac{8\pi}{3}|\langle a|\mathbf{p}|b\rangle|^2, \tag{8.8}$$

which follows because the sum of the two tensors $\mathbf{e_{k1}e_{k1}}$ and $\mathbf{e_{k2}e_{k2}}$ is $-\hat{\mathbf{k}}\hat{\mathbf{k}}$, where $\hat{\mathbf{k}}$ is the unit vector along $\mathbf{k}$. The angle average of $\hat{\mathbf{k}}\hat{\mathbf{k}}$ is $/3$, which leads directly to the result. Carrying out the steps mentioned leads to this:

$$w_{ba} = \frac{4}{3}\frac{e^2\omega}{\hbar c^3 m^2}|\langle a|\mathbf{p}|b\rangle|^2(n+1). \tag{8.9}$$

A transformation of the matrix element in (8.9) is possible using the commutator relation

$$\mathbf{p} = \frac{i}{\hbar}m[H_{\text{atom}}, \mathbf{r}], \tag{8.10}$$

which turns (8.9) into

$$w_{ba} = \frac{4}{3}\frac{e^2\omega^3}{\hbar c^3}|\langle a|\mathbf{r}|b\rangle|^2(n+1). \tag{8.11}$$

Finally we need to allow for degeneracy of the atomic states corresponding to the possible orientations of a state with nonzero total angular momentum. If the a state can have g_a different angular momentum projections m_a, and likewise for the b state, we get the transition rate for nonoriented atoms by averaging over m_b and summing on m_a:

$$w_{ba} = \frac{4}{3}\frac{\omega^3}{g_b\hbar c^3}\,_{ab}(n+1), \tag{8.12}$$

where $_{ab}$ is the electric dipole *line strength* defined by

$$_{ab} = \sum_{m_a, m_b}|\langle a\,m_a|e\mathbf{r}|b\,m_b\rangle|^2. \tag{8.13}$$

The occupation number n is the same as the number of photons per mode introduced earlier (see (6.16)). Thus the transition rate for emission is

$$w_{ba} = A_{ba} + B_{ba}I_\nu, \tag{8.14}$$

where A_{ba} and B_{ba} are two of the *Einstein coefficients*, the ones for spontaneous and stimulated emission, and are defined by

$$A_{ba} = \frac{32\pi^3}{3}\frac{\nu^3}{g_b\hbar c^3}\,_{ab}, \tag{8.15}$$

$$B_{ba} = \frac{A_{ba}}{4\pi\hbar\nu^3/c^2} = \frac{8\pi^2}{3g_b\hbar^2 c}\,_{ab}. \tag{8.16}$$

The absorption process can now be handled immediately. Nothing changes in the quantum mechanics except the factor involving n in the matrix element, which changes from $\sqrt{n+1}$ to $\sqrt{n}$ since the number in the initial state, n, is the larger of

the initial and final occupations, and that the averaging is over m_a and summation is taken over m_b. The transition rate turns out to be

$$w_{ab} = B_{ab} I_\nu, \tag{8.17}$$

with

$$B_{ab} = \frac{g_b}{g_a} B_{ba} = \frac{8\pi^2}{3g_a \hbar^2 c} \ _{ab}, \tag{8.18}$$

which defines the Einstein coefficient for absorption.

In a parcel of material in which state a is populated by N_a atoms per unit volume and state b by N_b atoms per unit volume, we can inquire what the net rate of transitions is between the two states for this parcel. We see that the rate is

$$N_a B_{ab} I_\nu - N_b (A_{ba} + B_{ba} I_\nu) \tag{8.19}$$

and that it would vanish if the intensity had the value

$$I_\nu = S_\nu = \frac{N_b A_{ba}}{N_a B_{ab} - N_b B_{ba}}. \tag{8.20}$$

This is therefore the atomic expression for the source function, since the definition of that is the intensity for which emission and absorption are in balance. Substituting the relations between the Einstein coefficients leads to an expression independent of the atomic constants,

$$S_\nu = \frac{2h\nu^3/c^2}{g_b N_a / g_a N_b - 1}. \tag{8.21}$$

We see that the source function will be the Planck function if and only if the Boltzmann relation is obeyed by the atomic state populations:

$$\frac{N_b}{N_a} = \frac{g_b}{g_a} \exp(-h\nu/kT). \tag{8.22}$$

The circumstance that the atomic state populations are determined by a balance of the rates of a variety of different processes, and that therefore the Boltzmann relation is not necessarily obeyed, leads to a source function that is not the same as the Planck function. When the equation of radiative transfer is solved using this source function, the intensity that is found does not agree with the Planck function either. This intensity may govern the rates of some of the atomic processes that, in turn, lead to the non-Boltzmann values of the state populations. Since the intensities are non-Planckian, the non-Boltzmann character of the populations is confirmed. The self-consistent calculation of atomic populations and the radiation field, neither of which agrees with thermodynamic equilibrium, is the subject of the theory of non-LTE, i.e., of systems not in local thermodynamic equilibrium.

The remaining quantities to discuss are the *oscillator strength* and the *absorption cross section*. The oscillator strength is defined by factoring out of B_{ab} all the dimensional quantities to leave a number of order unity; this is

$$f_{ab} = \frac{m\hbar cv}{2\pi e^2} B_{ab} = \frac{4\pi mv}{3g_a \hbar e^2} \quad ab = \frac{g_b}{g_a} \frac{mc^3}{8\pi^2 e^2 v^2} A_{ba}. \tag{8.23}$$

The emission oscillator strength is defined by a similar relation that is obtained from (8.23) by interchanging a and b and noting that the frequency changes sign; it is a negative quantity and obeys

$$f_{ba} = -\frac{g_a}{g_b} f_{ab}. \tag{8.24}$$

The usefulness of the oscillator strength stems from the *oscillator strength sum rule*, which says that the algebraic sum of all oscillator strengths, absorption and emission, beginning from a given state, equals the number of electrons in the atom. If the sum is restricted to certain subsets of the totality of states, sometimes there can be a sum rule relating the restricted sum to, for example, the number of outer-shell electrons. Absorption oscillator strengths, and sometimes dipole line strengths in atomic units of $(ea_0)^2$, are the quantities most often found in the tables.

The absorption transition rate given in (8.17) is based on the angle-average of the intensity. The part deriving from a particular solid angle $d\Omega$ would be $d\Omega/(4\pi)$ times the total. But $I_v d\Omega/(hv)$ is the photon particle flux per unit frequency in this solid angle, and therefore $hvB_{ab}/(4\pi)$ is related to the absorption cross section. But the transition rate is the total over frequency, while $I_v d\Omega/(hv)$ is the photon flux per unit frequency. Thus $hvB_{ab}/(4\pi)$ must be the frequency integral of the cross section:

$$\int dv\, \sigma_v = \frac{hv}{4\pi} B_{ab} = \frac{\pi e^2}{mc} f_{ab}. \tag{8.25}$$

The actual cross section σ_v is a sharply peaked function of frequency around $v = (E_b - E_a)/h$, but as we see there must be an inverse relation between the peak value of the cross section and its width in frequency, since its integral is fixed by the atomic constants. The width of the feature is actually produced by a variety of processes; some of these are the thermal motion of the atoms, the Stark effect produced by nearby positive ions, the perturbation by plasma electrons, the Zeemann effect of disordered magnetic fields, a small-scale random turbulent velocity in the gas, and on and on. These are all subsumed in a normalized distribution

function $\phi(\nu)$,

$$\int d\nu\, \phi(\nu) = 1. \tag{8.26}$$

Thus we have the actual cross section

$$\sigma_\nu = \frac{h\nu}{4\pi} B_{ab}\phi(\nu) = \frac{\pi e^2}{mc} f_{ab}\phi(\nu). \tag{8.27}$$

The absorptivity and emissivity follow from the Einstein coefficients and the line profile function. We note immediately that the absorptivity is the *difference* between absorption and stimulated emission, and that the emissivity comes from the spontaneous emission alone. The results are

$$k_\nu = \frac{h\nu}{4\pi}\phi(\nu)(N_a B_{ab} - N_b B_{ba})$$

$$= N_a \sigma_\nu \left(1 - \frac{N_b g_a}{N_a g_b}\right) \tag{8.28}$$

and

$$j_\nu = \frac{h\nu}{4\pi}\phi(\nu)N_b A_{ba}$$

$$= \frac{N_b g_a}{g_b}\sigma_\nu \frac{2h\nu^3}{c^2}. \tag{8.29}$$

In LTE, when the Boltzmann equation is obeyed, the relations become

$$k_\nu = N_a \sigma_\nu \left[1 - \exp(-h\nu/kT)\right] \tag{8.30}$$

and

$$j_\nu = N_a \sigma_\nu \frac{2h\nu^3}{c^2} \exp(-h\nu/kT) = k_\nu B_\nu. \tag{8.31}$$

8.3 Scattering

Our treatment of scattering follows Messiah (1961, 1962). Compton scattering and the Klein–Nishina cross section are discussed by Cox and Giuli (1968). Rayleigh scattering is considered by Sobel'man (1979). The simplest kind of scattering to consider is scattering by free electrons in a plasma, and in the nonrelativistic approximation this is Thomson scattering. No atom is involved in the process, and the initial and final states both include a free electron and a photon. The changes of energy and momentum of the photon are just balanced by the changes for the electron. In this case the $\mathbf{p} \cdot \mathbf{A}$ term in the interaction does not contribute anything since the matrix element vanishes for a free particle. We treat the $\mathbf{A}^2$ term in first

order perturbation theory, and select from the sums a destruction term for $\mathbf{k}_1\varpi_1$ and a creation term for $\mathbf{k}_2\varpi_2$. Let the initial electron momentum be $\hbar\mathbf{K}_1$ and the final momentum $\hbar\mathbf{K}_2$. The tricky bit is deciding on the appropriate density of states expression for Fermi's Golden Rule, and handling the matrix element, since

$$\int d^3\mathbf{r}\, \exp[i(\mathbf{k}_1 + \mathbf{K}_1 - \mathbf{k}_2 - \mathbf{K}_2)\cdot\mathbf{r}] = (2\pi)^3\delta(\mathbf{k}_1 + \mathbf{K}_1 - \mathbf{k}_2 - \mathbf{K}_2) \quad (8.32)$$

when taken over all space, where $\delta(\mathbf{k})$ is the 3-D Dirac delta function. This delta function ensures total momentum conservation for the scattering event. The strategy is something like this. If the electron states are normalized to one electron in the volume V, then each of the initial and final wavefunctions contains a factor $1/\sqrt{V}$ besides the free-wave exponential. We integrate over the factor $d^3\mathbf{K}_2/(2\pi)^3$ in the density of final states that accounts for the outgoing electron. That will use up one of the two factors of the integral (8.32). If momentum conservation is obeyed precisely, then the integral has the value V. Thus the second factor of the integral cancels with the factor $1/V$ that comes from the normalization of the electron states. Then we have to deal with the normalization of the photon states. We put a factor $Vk_2^2/(8\pi^3\hbar c)d\Omega_2$, the same as for spontaneous emission, in the density of final states to account for the outgoing photon. We in effect adjust the outgoing photon frequency to satisfy conservation of energy, having already adjusted the outgoing electron momentum to satisfy conservation of momentum. The transition rate has one surviving factor $1/V$ that comes from the expression for $\mathbf{A}$. One additional detail to notice is that the expansion of $\mathbf{A}^2$ contains the $a_{\mathbf{k}_1\varpi_1}a^\dagger_{\mathbf{k}_2\varpi_2}$ cross term twice, which becomes a factor 4 when the matrix element is squared.

After carrying out the substitutions as outlined, the following transition rate is found:

$$\left(\frac{e^2}{mc^2}\right)^2 (\mathbf{e}_{\mathbf{k}_1\varpi_1}\cdot\mathbf{e}_{\mathbf{k}_2\varpi_2})^2 \frac{k_2^2 c^3}{\omega_1\omega_2 V} n_{\mathbf{k}_1\varpi_1}(n_{\mathbf{k}_2\varpi_2} + 1)d\Omega_2. \quad (8.33)$$

As discussed above, the transition rate is proportional to the number of photons per mode in the initial state, and one plus the number of photons per mode in the final state. This will be used later in the detailed discussion of Compton scattering see (12.42). Since there is exactly one electron in the volume V, this transition rate should be the scattering cross section times the total incoming photon flux. The latter is $n_{\mathbf{k}_1\varpi_1}c/V$ since the photon states are normalized in the volume V. Thus we find a differential cross section

$$\frac{d\sigma}{d\Omega_2} = \left(\frac{e^2}{mc^2}\right)^2 (\mathbf{e}_{\mathbf{k}_1\varpi_1}\cdot\mathbf{e}_{\mathbf{k}_2\varpi_2})^2\frac{\omega_2}{\omega_1}(n_{\mathbf{k}_2\varpi_2} + 1), \quad (8.34)$$

in which the stimulated scattering factor $n_{\mathbf{k}_2 \varpi_2} + 1$ has been retained for the moment.

The factor $(\mathbf{e}_{\mathbf{k}_1 \varpi_1} \cdot \mathbf{e}_{\mathbf{k}_2 \varpi_2})^2$ in the differential cross section is interesting since it describes how polarized light is scattered by electrons, and also how polarized light is created by scattering unpolarized light. But for now we will average over the initial polarizations and sum on the final polarizations to get the differential cross section for unpolarized scattering. As above, we can replace $\mathbf{e}_{\mathbf{k}_1 \varpi_1} \mathbf{e}_{\mathbf{k}_1 \varpi_1}$ after summing over ϖ_1 with $-\hat{\mathbf{k}}_1 \hat{\mathbf{k}}_1$, do the same with $\mathbf{e}_{\mathbf{k}_2 \varpi_2} \mathbf{e}_{\mathbf{k}_2 \varpi_2}$, then form the fully contracted product of those two tensors. This operation yields $1 + (\hat{\mathbf{k}}_1 \cdot \hat{\mathbf{k}}_2)^2$, and therefore the unpolarized differential cross section is

$$\frac{d\sigma}{d\Omega_2} = \left(\frac{e^2}{mc^2}\right)^2 \frac{1 + (\hat{\mathbf{k}}_1 \cdot \hat{\mathbf{k}}_2)^2}{2} \frac{\omega_2}{\omega_1} (n_{\mathbf{k}_2 \varpi_2} + 1). \tag{8.35}$$

If Θ is the angle between the incoming and outgoing photon directions, then $\hat{\mathbf{k}}_1 \cdot \hat{\mathbf{k}}_2$ is the same as $\cos\Theta$, and the factor in the differential cross section is $(1 + \cos^2\Theta)/2$. This is the *phase function* for Thomson scattering. Its average over scattering angle is 2/3, which leads to the total Thomson scattering cross section

$$\sigma = \frac{8\pi}{3}\left(\frac{e^2}{mc^2}\right)^2 \frac{\omega_2}{\omega_1} (n_{\mathbf{k}_2 \varpi_2} + 1). \tag{8.36}$$

The difference between ω_2 and ω_1 is indeed very small, which is what we will show next. The standard Compton effect considers scattering of a photon from an electron at rest, in other words $\mathbf{K}_1 = 0$. The (relativistic) conservations laws for energy and momentum then require

$$\mathbf{K}_2 = \mathbf{k}_1 - \mathbf{k}_2, \tag{8.37}$$

$$E_2 - mc^2 = \hbar c(k_1 - k_2) \tag{8.38}$$

and the relativistic relation between E_2 and K_2 is

$$E_2^2 - (\hbar \mathbf{K}_2 c)^2 = (mc^2)^2. \tag{8.39}$$

Using the first two equations to eliminate $\mathbf{K}_2$ and E_2 from the third leads to the equation for the Compton effect

$$\frac{1}{k_2} - \frac{1}{k_1} = \frac{\hbar}{mc}(1 - \hat{\mathbf{k}}_1 \cdot \hat{\mathbf{k}}_2). \tag{8.40}$$

This tells us that the fractional change (reduction) in ω is approximately $\hbar\omega/(mc^2)$ times $(1 - \cos\Theta)$. Of course mc^2 is the electron rest energy, 511 keV. So except for hard x-rays and gamma-rays the fractional frequency shift is negligible.

There is a second contribution to the frequency shift when the initial electron is not at rest, but has a random velocity as in a Maxwellian distribution. The Doppler

shifts to the rest frame of the incoming electron and back to the laboratory frame again after scattering lead to a random up or down shift of the photon frequency by an amount of order $\omega(1 - \cos \Theta)\sqrt{2kT/(mc^2)}$. Although $\sqrt{2kT/(mc^2)}$ is usually small, it is not nearly as small as $\hbar\omega/(mc^2)$, so in practical cases these up and down shifts are larger than the Compton shift. Even so, they can generally be neglected for scattering by electrons whose temperature is in the eV range. At the temperature of the solar corona, however, around 150 eV, the Doppler shift is about 2.4%, and is responsible for washing out the photospheric absorption lines in the scattered spectrum observed from the corona in eclipse or with a coronagraph.

For ordinary purposes, then, we can drop the factor ω_2/ω_1 in the cross section, which therefore also means that stimulated in-scattering will precisely cancel stimulated out-scattering, and the factor $1 + n$ can be discarded as well. This gives the common Thomson cross section

$$\sigma_T = \frac{8\pi}{3}\left(\frac{e^2}{mc^2}\right)^2. \tag{8.41}$$

For completeness we will note that when the photon energy is no longer small compared with mc^2, in the domain of the Compton effect in other words, the cross section is less than the Thomson value and is given by the Klein–Nishina formula

$$\sigma_{KN} = \frac{3}{4}\sigma_T\left\{\frac{1+u}{u^3}\left[\frac{2u(1+u)}{1+2u} - \log(1+2u)\right] + \frac{\log(1+2u)}{2u} - \frac{1+3u}{(1+2u)^2}\right\}, \tag{8.42}$$

where $u = h\nu/mc^2$, provided the scattering electron is initially at rest; the cross section is shown in Figure 8.1. For moving electrons the cross section in any
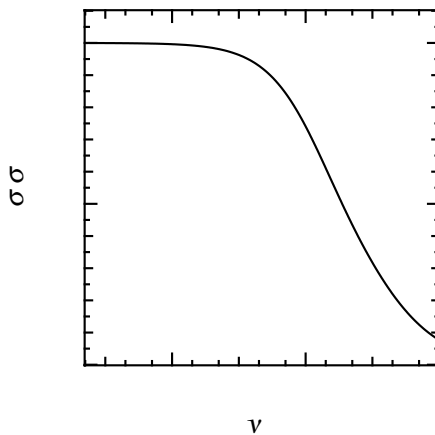

Fig. 8.1 Relativistic (Klein–Nishina) Compton cross section in terms of the Thomson cross section vs photon frequency in keV.

particular direction must be found by transforming the photon frequency into the rest frame of the electron using (6.9), evaluating the Klein–Nishina cross section, then transforming back to the fixed frame with (6.23). Some of the implications of an exact treatment of Compton scattering are considered in Section 12.3.

The other kind of scattering we want to consider is scattering by the electrons bound in atoms. This is called Rayleigh or Raman scattering depending on whether the initial and final atomic states are the same or different. Because the bound-state wave functions occupy a finite volume, unlike the free electron states, the subtleties of the density of states and delta functions are not required. What is required is to find the effective interaction matrix element by combining the $\mathbf{A}^2$ term in first order with the $\mathbf{p} \cdot \mathbf{A}$ term in second order. We will spare the details and just quote the result. This is simple in the Rayleigh case where states a and b are the same and if the total angular momentum is $J = 0$ in the initial state a. The differential cross section for specific polarization states in that case is

$$\frac{d\sigma}{d\Omega} = \left(\frac{e^2}{mc^2}\right)^2 \left| \sum_c \frac{\omega^2 f_{ac}}{\omega_{ac}^2 - \omega^2} \right|^2 (\mathbf{e}_{\mathbf{k}_1 \varpi_1} \cdot \mathbf{e}_{\mathbf{k}_2 \varpi_2})^2, \tag{8.43}$$

where the frequencies of the scattered photon and the initial photon must be the same in this case, $\omega_1 = \omega_2 = \omega$. The summation is taken over all the members c of a complete set of atomic states, and ω_{ac} is the excitation energy from state a to the intermediate state c. The cross section can also be written as

$$\frac{d\sigma}{d\Omega} = k^4 [\alpha(\omega)]^2 (\mathbf{e}_{\mathbf{k}_1 \varpi_1} \cdot \mathbf{e}_{\mathbf{k}_2 \varpi_2})^2, \tag{8.44}$$

where $\alpha(\omega)$ is the AC polarizability of the atom in the state a:

$$\alpha(\omega) = \frac{e^2}{m} \sum_c \frac{f_{ac}}{\omega_{ac}^2 - \omega^2}. \tag{8.45}$$

We observe that Rayleigh scattering, like Thomson scattering, has the phase function $(1 + \cos^2 \Theta)/2$, which goes by the generic title dipole phase function.

You see that at low frequency, when the polarizability tends to the constant DC value, the scattering cross section becomes very small, following then the λ^{-4} law for optical Rayleigh scattering. This comes about because there is almost complete cancellation between the second order $\mathbf{p} \cdot \mathbf{A}$ term and the first order $\mathbf{A}^2$ term in the interaction. At high frequency the cross section becomes the same as the Compton cross section, because the fact that the electrons are bound to an atom is irrelevant when the photon momentum is large enough. As a matter of fact, (8.43) is inappropriate when the photon wavelength becomes comparable to the size of the atom. The dipole approximation breaks down, and the $\mathbf{A}^2$ interaction term should then be multiplied by a structure factor that depends on the momentum transfer, $\mathbf{k}_2 - \mathbf{k}_1$.

As the wavelength decreases, the momentum transfer increases and the structure factor becomes very small, which makes this part of the interaction negligible. At the same time a Raman scattering term becomes important that corresponds to leaving the atom in a final state with an ejected electron that has the momentum $\hbar(\mathbf{k}_1 - \mathbf{k}_2)$. If the atom has N electrons, then at photon energies large compared with all the atomic binding energies but small compared with $\hbar c/r$, all N electrons add coherently in the polarizability, which makes the scattering cross section N^2 times as large as that for a single electron. But when the photon energy is large compared with $\hbar c/r$ the Compton scattering contributions of the electrons add incoherently, so the cross section is N times that for a single electron.

8.4 Photoionization and recombination

When the final state of the photoabsorption process considered earlier belongs to a continuum, as it does when a photoelectron is ejected, the calculation needs to be modified since the density of states factor can be based on the electron continuum instead of the continuum of absorbed photon energies. This discussion is partly based on Sobel'man (1979). Since there is a reciprocal relation between the free-wave normalization and the density of states, we will make a specific normalization choice for the free waves $\psi(\mathbf{r})$, which is

$$\psi(\mathbf{r}) = \psi_{\mathbf{K}}(\mathbf{r}) \sim \exp(i\mathbf{K} \cdot \mathbf{r}) \quad \text{for } r \to \infty, \tag{8.46}$$

which corresponds to a unit density of free electrons. The corresponding density of final states per unit energy is

$$\rho = \frac{mK \, d\Omega_{\mathbf{K}}}{(2\pi)^3 \hbar^2}, \tag{8.47}$$

and the incoming photon flux is $n_{\mathbf{k}\varpi} c / V$. With these replacements the transition rate for photoabsorption becomes

$$
\begin{aligned}
w_{ab\mathbf{K}} &= \frac{2\pi}{\hbar} \left(\frac{e}{mc} \right)^2 \frac{2\pi \hbar c^2}{\omega V} |\langle b\mathbf{K}| \exp(i\mathbf{k} \cdot \mathbf{r}) \mathbf{p} \cdot \mathbf{e}_{\mathbf{k}\varpi} |a\rangle|^2 n_{\mathbf{k}\varpi} \frac{mK \, d\Omega_{\mathbf{K}}}{(2\pi)^3 \hbar^2} \\
&= \frac{1}{2\pi} \frac{e^2 K}{\hbar^2 m V \omega} |\langle b\mathbf{K}| \exp(i\mathbf{k} \cdot \mathbf{r}) \mathbf{p} \cdot \mathbf{e}_{\mathbf{k}\varpi} |a\rangle|^2 n_{\mathbf{k}\varpi},
\end{aligned}
\tag{8.48}
$$

which gives the differential cross section upon being divided by the flux times $d\Omega_{\mathbf{K}}$:

$$\frac{d\sigma_{PI}}{d\Omega_{\mathbf{K}}} = \frac{1}{2\pi} \frac{e^2 K}{\hbar^2 mc\omega} |\langle b\mathbf{K}| \exp(i\mathbf{k} \cdot \mathbf{r}) \mathbf{p} \cdot \mathbf{e}_{\mathbf{k}\varpi} |a\rangle|^2. \tag{8.49}$$

In the dipole approximation we can drop the exponential in the matrix element and then use the commutator relation (8.10) to obtain

$$\frac{d\sigma_{PI}}{d\Omega_{\mathbf{K}}} = \frac{1}{2\pi} \frac{me^2 Kk}{\hbar^2} |\langle b\mathbf{K}|\mathbf{r}\cdot\mathbf{e}_{\mathbf{k}\varpi}|a\rangle|^2. \tag{8.50}$$

In order to get the total cross section corresponding to this differential cross section it is most convenient to expand in spherical waves for the final state:

$$\psi_{\mathbf{K}}(\mathbf{r}) = \frac{4\pi}{K} \sum_{lm} i^l (Y_l^m(\theta_{\mathbf{K}}, \phi_{\mathbf{K}}))^* \psi_{Klm}(\mathbf{r}) \tag{8.51}$$

with

$$\psi_{Klm}(\mathbf{r}) = Y_l^m(\theta, \phi) R_{Kl}(r). \tag{8.52}$$

Here θ and ϕ are the angular coordinates of the ejected electron, and $\theta_{\mathbf{K}}$ and $\phi_{\mathbf{K}}$ are the coordinates for the direction of $\mathbf{K}$. The radial function has the asymptotic form

$$R_{Kl}(r) \sim \frac{\sin(Kr - l\pi/2 + \delta)}{r}. \tag{8.53}$$

The result of inserting the expansion for each factor $\psi_{\mathbf{K}}(\mathbf{r})$ and integrating over $d\Omega_{\mathbf{K}}$, where the orthogonality of the $Y_l^m(\theta_{\mathbf{K}}, \phi_{\mathbf{K}})$ can be used, is

$$\sigma_{PI} = 8\pi \frac{me^2 k}{\hbar^2 K} \sum_{lm} |\langle bKlm|\mathbf{r}\cdot\mathbf{e}_{\mathbf{k}\varpi}|a\rangle|^2. \tag{8.54}$$

The average over the polarization modes introduces a factor $(\quad - \hat{\mathbf{k}}\hat{\mathbf{k}})/2$. Averaging over the direction of the incoming photon, or, which is equivalent, averaging over the m_a values for the initial state and summing over the m_b values for the residual ion state, and furthermore summing over the two possible free-electron spin states, allows us to replace this tensor with $/3$. That gives finally

$$\sigma_{PI} = \frac{8\pi}{3} \frac{me^2 k}{g_a \hbar^2 K} \sum_{lmm_s m_a m_b} |\langle bm_b Klmm_s|\mathbf{r}|am_a\rangle|^2. \tag{8.55}$$

The cross section in (8.55) is for the process of photoionization. For a simple atom such as hydrogen the values of K and the matrix elements are of order unity when expressed in atomic units ($\hbar = m = e = 1$), but $k = \omega/c$, and while ω is of order unity in atomic units, $c = 1/\alpha \approx 137$ in those units. Thus the cross section is of order $\alpha\pi a_0^2$, where a_0 is the Bohr radius, the atomic unit of length. This makes the cross section 10^{-18} cm^2 or less. This is still much larger than the Thomson cross section, which is $8\alpha^4/3 \approx 10^{-8}$ times πa_0^2, or 6.65×10^{-25} cm^2.

The inverse process, radiative capture or radiative recombination, is described by exactly the same matrix element, but the density of final states should be that for the photon state, not the free electron, and the flux by which the rate is divided to obtain the cross section is the free-electron flux, not the photon flux. Making these adjustments leads to this differential cross section for the radiative capture process:

$$\frac{d\sigma_{RC}}{d\Omega_{\mathbf{k}}} = \frac{1}{2\pi} \frac{me^2 k^3}{\hbar^2 K} |\langle b\mathbf{K}|\mathbf{r} \cdot \mathbf{e}_{\mathbf{k}\varpi}|a\rangle|^2. \tag{8.56}$$

Putting in the spherical state expansion in place of the plane wave state, summing over the two polarizations and forming the average over incoming electron direction and the angle integral of the outgoing photon direction, as well as summing over the possible values of m_a and averaging over the possible values of m_b and of the free-electron spin m_s, as before, gives the result for the total cross section for radiative capture:

$$\sigma_{RC} = \frac{8\pi}{3} \frac{me^2 k^3}{g_b \hbar^2 K^3} \sum_{lmm_s m_a m_b} |\langle bm_b K lmm_s|\mathbf{r}|am_a\rangle|^2. \tag{8.57}$$

We have not carried along the factor $1 + n_{\mathbf{k}\varpi}$ that enters from the matrix element of $a_{\mathbf{k}\varpi}^\dagger$, but it should be included as well to give the total recombination including stimulated recombination. The stimulation factor can as before be expressed as $1 + I_\nu/(2h\nu^3/c^2)$, and is included as a subtraction in the absorptivity for photoionization. The cross section σ_{RC} is for spontaneous recombination.

Evidently the reciprocity relation between photoionization and radiative capture or radiative recombination is

$$\frac{\sigma_{RC}}{\sigma_{PI}} = \frac{k^2}{K^2} \frac{g_a}{g_b} = \frac{h^2\nu^2}{m^2 v^2 c^2} \frac{g_a}{g_b}. \tag{8.58}$$

This reciprocity relation is called the *Milne relation* and it is the equivalent for photoionization/recombination of the relation between the Einstein A and B coefficients. The statistical weight ratio here is simply that between the initial atom state and the residual ion state; the electron spin factor 2 has been canceled by a factor 2 for the number of photon polarization states. The recombination cross section is of order $\alpha^2 \approx 10^{-4}$ times the photoionization cross section.

If the intensity I_ν equals the source function S_ν for photoionization then the rate of photoionizations by photons in a range $[\nu, \nu + d\nu]$ must balance the rate of radiative recombinations due to free electrons in a velocity range $[v, v + dv]$, where the frequencies and velocities are in correspondence according to $h\nu = E_b - E_a + mv^2/2$. The relation of $d\nu$ and dv will therefore be $h\,d\nu = mv\,dv$. The photon flux in $d\nu$ with $I_\nu = S_\nu$ is $4\pi S_\nu/d\nu/(h\nu)$. The free-electron flux in dv

comes from the Maxwellian velocity distribution, and is

$$\sqrt{\frac{2}{\pi}} \left(\frac{m}{kT}\right)^{3/2} N_e v^3 dv\, e^{-mv^2/2kT}, \tag{8.59}$$

in which N_e is the total density of free electrons. The recombination rate has to include the stimulation factor corresponding to S_ν. Therefore the balance equation is

$$N_a \sigma_{PI} \frac{4\pi}{h\nu} S_\nu\, d\nu = N_b \sigma_{RC} \sqrt{\frac{2}{\pi}} \left(\frac{m}{kT}\right)^{3/2} N_e v^3 dv\, e^{-mv^2/2kT} (1 + c^2 S_\nu/(2h\nu^3)). \tag{8.60}$$

The solution of this equation for S_ν is

$$S_\nu = \frac{2h\nu^3/c^2}{\mathcal{F} - 1}, \tag{8.61}$$

where $\mathcal{F}$ is defined by the expression

$$\begin{aligned} \mathcal{F} &= \frac{N_a \sigma_{PI} (8\pi\nu^2/c^2) d\nu}{N_b \sigma_{RC} \sqrt{2/\pi} (m/kT)^{3/2} N_e v^3 dv\, \exp(-mv^2/2kT)} \\ &= \frac{N_a}{N_e N_b} \frac{2g_b}{g_a} \left(\frac{2\pi mkT}{h^2}\right)^{3/2} e^{mv^2/2kT}. \end{aligned} \tag{8.62}$$

This expression for S_ν will become the Planck function, as it must in thermal equilibrium, if $\mathcal{F} = \exp(h\nu/kT)$, and therefore if

$$\frac{N_e N_b}{N_a} = \frac{2g_b}{g_a} \left(\frac{2\pi mkT}{h^2}\right)^{3/2} e^{-(E_b - E_a)/kT}, \tag{8.63}$$

which is Saha's equation for ionization balance in thermal equilibrium.

For the ideal nondegenerate and nonrelativistic electron gas, the chemical potential, the Gibbs free energy per particle, in this case per free electron, is given by

$$\mu_e = kT \log\left[\frac{N_e}{2} \left(\frac{h^2}{2\pi mkT}\right)^{3/2}\right]. \tag{8.64}$$

The factor 2 dividing N_e in (8.64) arises from the spin multiplicity of the electron. In terms of the chemical potential Saha's equation becomes

$$\frac{N_b}{N_a} = \frac{g_b}{g_a} e^{-(E_b - E_a + \mu_e)/kT}. \tag{8.65}$$

In this form the equation remains valid even if the electrons are degenerate, provided they can still be treated as an ideal Fermi gas. The nonrelativistic formula

connecting μ_e to the temperature and electron density becomes

$$\frac{2}{\sqrt{\pi}} F_{1/2}\left(\frac{\mu_e}{kT}\right) = \frac{N_e}{2}\left(\frac{h^2}{2\pi mkT}\right)^{3/2}, \tag{8.66}$$

where the function $F_{1/2}(x)$ is the Fermi function defined by

$$F_{1/2}(x) = \int_0^\infty \frac{t^{1/2}\, dt}{e^{t-x}+1}. \tag{8.67}$$

For a hydrogen-like system the initial state for photoionization is a hydrogenic wavefunction with quantum numbers n and l, and the final state is a Coulomb wave. The exact calculation of the photoionization cross section in this case gives

$$\sigma_{PI}(\nu) = \frac{64}{3\sqrt{3}}\alpha\pi a_0^2 \frac{ng_{II}}{Z^2}\left(\frac{\nu_0}{\nu}\right)^3, \tag{8.68}$$

(see Allen (1973)) where Z is the charge of the residual ion ($Z = 1$ for hydrogen), α is the fine-structure constant, $1/137.036$, g_{II} is the bound–free Gaunt factor that depends on n, l, and ν. The frequency ν_0 is the edge value for level n, Z^2/n^2 times the Rydberg frequency. The constant $64/(3\sqrt{3})\alpha\pi a_0^2$ is 7.90707×10^{-18} cm^2. The Gaunt factor is not *very* far from 1, especially when averaged over l at a given n. Replacing it with 1 is an approximation (Kramer's law) that is qualitatively correct. Accurate tables and subroutines for it exist today. The hydrogenic results can be extended in an approximate way to nonhydrogenic ions by using in place of Z in the hydrogenic formulae the expression $Z - N + 1$ in which N is the number of bound electrons.

The total rate coefficient for radiative recombination in a plasma in which the electrons have a Maxwellian distribution at a temperature T can be calculated, using the Milne relation, as an integral over the photoionization cross section times the Planck distribution corrected for stimulated emission. That is, the rate of spontaneous recombinations per unit volume is given by

$$N_e N_b \alpha_{RR}(T) = N_a \int_{\nu_0}^\infty d\nu\, \sigma_{PI}(\nu)\frac{8\pi\nu^2}{c^2}\exp(-h\nu/kT), \tag{8.69}$$

where it is understood that the Saha equation is to be used to express N_a in terms of $N_e N_b$. Here $\alpha_{RR}(T)$ is the recombination coefficient. When the Saha equation is substituted the expression for it is

$$N_e \alpha_{RR}(T) = \int_{\nu_0}^\infty d\nu\, \sigma_{PI}(\nu)\frac{8\pi\nu^2}{c^2}\exp\left(\frac{\mu_e - h\nu}{kT}\right). \tag{8.70}$$

In the nondegenerate case this becomes

$$\alpha_{RR}(T) = \frac{g_a}{2g_b}\left(\frac{h^2}{2\pi mkT}\right)^{3/2}\int_{\nu_0}^{\infty}d\nu\,\sigma_{PI}(\nu)\frac{8\pi\nu^2}{c^2}\exp(-h\nu/kT). \quad (8.71)$$

The recombination coefficient to a hydrogen-like ion, for the principal quantum number n with all the l values summed, is given by

$$\alpha_n(T) = \frac{2.06505\times10^{-11}}{\sqrt{T}}\frac{\bar{g}_{II}}{n}[X_n e^{X_n}E_1(X_n)] \quad \text{cm}^3\,\text{s}^{-1}, \quad (8.72)$$

where $X_n = Z^2 Ryd/(n^2 kT)$ is the binding energy of level n in units of kT. The expression in the brackets in (8.72) is about unity for levels more tightly bound than kT and tends to 0 as $1/n^2$ as n increases above that point. This means that at low temperature there are sizeable contributions to the total recombination from many values of n. The total recombination rate varies with T close to the power $T^{-1/2}$.

8.5 Free–free absorption – bremsstrahlung

Free–free absorption, also called inverse bremsstrahlung, is the next step past bound–free absorption, which is another name for photoionization. Here not only does the final state of the process have a free electron, but so does the initial state. So the process has a formula like this:

$$e + X + h\nu \rightarrow X' + e'. \quad (8.73)$$

Most often the case we are interested in is when the final state of the atom X is the same as the initial state, and so the energy of the photon goes into the energy of the outgoing electron. (The case that X changes state too is an example of a two-electron transition, i.e., two or more electrons have to change from one orbital to another, and since the radiative interaction $\mathbf{p}\cdot\mathbf{A}$ is a one-particle operator, such transitions do not occur without configuration mixing, which makes them much less likely.)

The quantum mechanics of this process is only altered a little from that for photoionization. We expect a cross section for absorbing the photon that is proportional to the density of electrons with the initial momentum $\hbar\mathbf{K}_1$. We get the cross section for unit density by taking the initial free-electron wave-function to be $\exp(i\mathbf{K}_1\cdot\mathbf{r})$. The density of final states in energy and the photon flux are unchanged. The total cross section for all angles of the photon and electrons is found as before by introducing expansions (8.51) in spherical waves for both the

incoming and outgoing electrons. The result is

$$\sigma(K_1\omega; K_2) = \frac{16\pi^2}{3} \frac{me^2k}{g_a\hbar^2 K_1^2 K_2}$$
$$\times \sum_{m_a m'_a l m m_s l' m' m'_s} |\langle a m'_a K_2 l' m' m'_s |\mathbf{r}| a m_a K_1 l m m_s\rangle|^2. \quad (8.74)$$

For the bremsstrahlung process the colliding particle is an electron, and therefore we are seeking a cross section for electron collisions, but since there are two continuously distributed particles in the final state, we can assign a range $d\omega$ to the photon frequency and find the differential cross section for that range. What we find is

$$\frac{d\sigma(K_2; K_1\omega)}{d\omega} = \frac{16}{3} \frac{m^2 e^2 k^3}{g_a\hbar^3 K_1 K_2^3}$$
$$\times \sum_{m_a m'_a l m m_s l' m' m'_s} |\langle a m'_a K_2 l' m' m'_s |\mathbf{r}| a m_a K_1 l m m_s\rangle|^2. \quad (8.75)$$

The reciprocity relation between $\sigma(K_1\omega; K_2)$ and $d\sigma(K_2; K_1\omega)/d\omega$ is that $\sigma(K_1\omega; K_2)$ times the electron density times the fraction of the electrons that have kinetic energy lying between $E_1 = \hbar^2 K_1^2/2m$ and $E_1 + dE$ times the photon flux lying in the range ω to $\omega + d\omega$ should be equal, in thermodynamic equilibrium, to $d\sigma(K_2; K_1\omega)/d\omega$ times $d\omega$ times the electron density times the fraction of the electrons that have kinetic energy lying between $E_2 = \hbar^2 K_2^2/2m$ and $E_2 + dE$ times the velocity $\hbar K_2/m$.

There is a problem with the matrix element that appears in (8.74) and (8.75), and that is that the integral of r times the product of two Coulomb waves does not converge in $r \to \infty$, but oscillates with increasing amplitude. So rather than using the commutator relation to express the matrix element of $\mathbf{p}$ in terms of the matrix element of $\mathbf{r}$, we should go the other way, and express the matrix element of $\mathbf{p}$ in terms of the matrix element of the central force that acts on the electron. If we now let V be the spherically symmetric potential energy for the initial and final free electrons, forgetting about its previous meaning as the volume of a box, the commutator relation we need is

$$[H, \mathbf{p}] = -\frac{\hbar}{i} \frac{dV}{dr} \hat{\mathbf{r}}, \quad (8.76)$$

so that an alternative form of (8.74) is

$$\sigma(K_1\omega; K_2) = \frac{16\pi^2}{3} \frac{e^2}{g_a m \hbar^2 c \omega^3 K_1^2 K_2}$$

$$\times \sum_{m_a m_a' l m m_s l' m' m_s'} \left| \left\langle a m_a' K_2 l' m' m_s' \left| \frac{dV}{dr} \hat{\mathbf{r}} \right| a m_a K_1 l m m_s \right\rangle \right|^2, \quad (8.77)$$

and a similar form exists for $d\sigma(K_2; K_1\omega)/d\omega$. At large r, dV/dr varies as r^{-2}, which ensures convergence of the radial integral.

   If the target ion, or the residual ion in the final state, is a bare nucleus, then we have hydrogen-like initial and final states, which for free electrons are Coulomb waves. Like the bound–bound and bound–free transitions, the free–free transitions can be expressed in terms of a Gaunt factor. We let Z be the charge of the target ion, represent the frequency in terms of ν instead of ω, and set $\hbar K_1/m = v_1$. We find the following result for the absorption cross section:

$$\sigma(v_1\omega; v_2) = \frac{4\pi}{3\sqrt{3}} \frac{Z^2 e^6 g_{III}}{hcm^2 v_1 \nu^3}. \quad (8.78)$$

We must keep in mind that this is the cross section for photoabsorption given that there is one electron per unit volume with the velocity v_1. The quantity g_{III} is the free–free gaunt factor, and is generally around unity. It is given by a formula very similar to the one for the bound–free gaunt factor g_{II}, and also a bound–bound Gaunt factor g_I we have not discussed. When the free–free absorption for a thermal plasma is the quantity we want, then we have to average (8.78) over the Maxwellian distribution for v_1. The average of $1/v_1$ becomes $\sqrt{2m/\pi kT}$. As a result the absorptivity at frequency ν by the free–free process, but not yet corrected for stimulated emission, for ions that have a charge Z and an ionic density N_i, is given by

$$k_{\nu,ff} = \frac{4\sqrt{2\pi}}{3\sqrt{3}} \frac{Z^2 e^6 \bar{g}_{III}}{hc\sqrt{m^3 k}\nu^3} \frac{N_e N_i}{\sqrt{T}}$$

$$= 3.69234 \times 10^8 \frac{Z^2 \bar{g}_{III}}{\sqrt{T}\nu^3} N_e N_i, \quad (8.79)$$

where in the numerical form the densities are in cm^{-3}, the temperature is in K, the frequency is in Hz and the result is in cm^{-1}.

   The radio-frequency case, i.e., when ν is small, is an exception to the general rule that the Gaunt factor is close to unity. An expression that covers this case is

the following, from Allen (1973):

$$g_{III} \approx \max \left[1, \frac{\sqrt{3}}{\pi} \log \left(\frac{4\pi v/\nu}{\max(Ze^2/mv^2, \hbar/mv)} \right) \right], \qquad (8.80)$$

which becomes logarithmically large when $v \to 0$. Here v is the final electron velocity. In the classical picture this logarithm, as in other Coulomb integrals, comes from an integral over the impact parameter b for electron–ion trajectories that to begin with looks like

$$\int_0^\infty \frac{db}{b},$$

which obviously diverges unless cutoffs $b_{\min}$ and $b_{\max}$ are applied. Quantum mechanics supplies one value for $b_{\min}$, which is $\hbar/mv$, since the quantization of angular momentum is equivalent to quantizing b in units of $\hbar/mv$. An alternative lower limit comes from the geometry of the hyperbolic classical orbits: when b is larger than Ze^2/mv^2 the deflection of the colliding electron is by an angle less than $\pi/2$ and therefore the general direction of the acceleration is consistent through the entire collision. But when b is smaller than Ze^2/mv^2 the orbit tends to double back on itself. The result is that the radiation of the second half of the collision partly cancels that from the first half. This cancellation factor allows the integral to converge. The correct $b_{\min}$ is approximately equal to whichever is larger of $\hbar/mv$ and Ze^2/mv^2. The quantum limit is effective at very high velocity and the $\pi/2$ deflection limit applies at somewhat lower velocity. The upper cutoff is less obvious. The case of an isolated ion, far from any other ion, is treated with the quantum mechanical method as sketched above, and the upper cutoff comes from the requirement that the collision produce some radiation at the frequency ν; if b is too large, then the time-dependent fields produced by the acceleration of the electron do not have an appreciable component at frequency ν. The collision time at impact parameter b is of order b/v and therefore the Fourier spectrum of the radiated energy cuts off above $\nu = \omega/2\pi = v/2\pi b$. These results for $b_{\min}$ and $b_{\max}$ lead to (8.80) when it is further observed that the classical arguments involving b fail altogether if they lead to a Gaunt factor less than unity, which is the typical non-classical value. It should be noted that the exact quantum mechanical calculations of the free–free Gaunt factor, based on Coulomb wave functions, implicitly include the cutoffs described in this paragraph; these accurate results are roughly approximated by (8.80).

In a denser plasma it can happen that the cutoff $v/2\pi\nu$ is larger than the Debye length, r_D. Since the target ion's field is considered fully shielded at $r > r_D$, the integral should be cut off at that value. This will happen for $\omega < v/r_D$. If v is

taken to be $\sqrt{kT/m}$ then the frequency below which the Debye limit is in effect is $\sqrt{kT/mr_D^2} \approx \omega_{pe}$, the electron plasma frequency. When the frequency is the same order as the electron plasma frequency the effects of plasma dispersion must also be considered, and we have to deal with a nonunit refractive index. We will touch on this topic some more below.

8.6 Opacity calculations

For the astrophysical plasma the total absorptivity is obtained by adding up the processes outlined in the last four sections. The bound–bound (Section 8.2) bound–free (Section 8.4) and free–free (Section 8.5) cross sections are evaluated for each of the possible states of all the ion species in the plasma, multiplied by the ion density appropriate for that state, then summed. This sum is corrected for stimulated emission, in local thermodynamic equilibrium, by multiplying it by $1 - \exp(-h\nu/kT)$. Thomson scattering contributes an amount $N_e \sigma_T$ to the absorptivity. Rayleigh scattering, like bound–bound absorption, is the sum of ion state densities multiplied by the Rayleigh scattering cross section. The total of Thomson and Rayleigh scattering is added to the absorptivity as-is, since the stimulated scattering correction is negligible. The total absorptivity (dimension inverse length) is converted to opacity (dimension length²/mass) by dividing by the mass density ρ. Thus the opacity, denoted by κ_ν, is given by an expression like

$$\kappa_\nu \rho = \left[\sum_{ijk} N_{ij} \frac{\pi e^2}{mc} f_{jk} \phi_{jk}(\nu) + \sum_{ij} N_{ij} \sigma_{ij}^{PI}(\nu) \right.$$

$$\left. + \sum_{ij} N_{ij} N_e \bar{\sigma}_{ij}(\nu; \nu'\nu) \right] \left(1 - e^{-h\nu/kT} \right) + N_e \sigma_T + \sum_{ij} N_{ij} \sigma_{ij}^{RS}(\nu), \quad (8.81)$$

in which the index i denotes a particular charge state for a particular element and the index j denotes a particular electronic excitation state of that ion. The quantity $\bar{\sigma}_{ij}(\nu; \nu'\nu)$ is the thermally-averaged free–free absorption cross section for a unit density of colliding electrons, and $\sigma_{ij}^{RS}(\nu)$ is the Rayleigh scattering cross section for ions i in excitation state j. The Rayleigh term is most often approximated using the ground-state contribution alone. Opacity calculations in general, and the construction of mean opacities, are discussed by Cox and Giuli (1968).

As indicated earlier, diffusion theory leads to a frequency-integrated flux that is proportional to the gradient of the temperature, *viz.*,

$$\mathbf{F} = -\frac{16\sigma T^3}{3\kappa_R \rho} \nabla T, \quad (8.82)$$

where here we have replaced the absorptivity in terms of the opacity. To repeat how we have arrived at this formula, we have the diffusion formula for the mono-

chromatic flux,

$$\mathbf{F}_\nu = -\frac{4\pi}{3\kappa_\nu\rho}\nabla B_\nu(T) = -\frac{4\pi}{3\kappa_\nu\rho}\frac{dB_\nu}{dT}\nabla T, \tag{8.83}$$

which we integrate over ν. The integral of the derivative of the Planck function is just the derivative of the integral, so

$$\int_0^\infty d\nu\, \frac{dB_\nu(T)}{dT} = \frac{d}{dT}\int_0^\infty d\nu\, B_\nu(T) = \frac{d}{dT}\left(\frac{\sigma T^4}{\pi}\right) = \frac{4\sigma T^3}{\pi}. \tag{8.84}$$

The Rosseland mean opacity κ_R is defined by

$$\frac{1}{\kappa_R} = \frac{\displaystyle\int_0^\infty d\nu\, \frac{1}{\kappa_\nu}\frac{dB_\nu}{dT}}{\displaystyle\int_0^\infty d\nu\, \frac{dB_\nu}{dT}}, \tag{8.85}$$

and combining the last three results gives the desired expression. We also repeat for emphasis that the Rosseland mean is computed from the sum of absorption and scattering in which the absorption part is corrected for stimulated emission.

We also may sometimes want a mean opacity with which to express the total emission rate by the material, as in (4.43). If there is a mixture of absorption and scattering, so that $k_\nu = k_\nu^a + k_\nu^s$, and if the source function for the absorption part is B_ν and that for the scattering part is J_ν, as discussed in the previous chapter, then the expression for the energy coupling rate g^0 reduces to this:

$$\begin{aligned}
g^0 &= \int d\nu \int d\Omega \left[k_\nu^a B_\nu + k_\nu^s J_\nu - (k_\nu^a + k_\nu^s)I_\nu\right] \\
&= 4\pi \int d\nu \left[k_\nu^a B_\nu + k_\nu^s J_\nu - (k_\nu^a + k_\nu^s)J_\nu\right] \\
&= 4\pi \int d\nu\, k_\nu^a (B_\nu - J_\nu).
\end{aligned} \tag{8.86}$$

We have assumed that the absorptivity is isotropic, so this reduction is appropriate for the comoving frame. What we see is that the scattering process disappears from the net energy exchange rate. To be more precise, the energy exchange due to scattering comes from the terms, neglected here, that allow the frequency of a photon to change in the scattering process. We focus now on the B_ν term in the integral; this is from the emission rate. If we define the Planck mean opacity by

$$\kappa_P = \frac{\displaystyle\int_0^\infty d\nu\, \kappa_\nu B_\nu}{\displaystyle\int_0^\infty d\nu\, B_\nu}, \tag{8.87}$$

then the energy emission rate is

$$4\pi\kappa_P\rho B = 4\sigma\kappa_P\rho T^4. \tag{8.88}$$

Unfortunately, the spectral distribution J_ν is not generally known unless a detailed multifrequency calculation is done, so the integral of the absorption term cannot be evaluated exactly. What might be done in a gray approximation is to assume that the spectrum of J_ν has the same shape as that of B_ν, and hope for the best. Thus the same mean, the Planck mean, might be taken for both terms. If this is done, the result for the energy coupling (in the comoving frame, in general) is

$$g^0 = 4\pi\kappa_P\rho(B - J), \tag{8.89}$$

where B is $\sigma T^4/\pi$ and J stands for the frequency integral $\int d\nu\, J_\nu$. This is the relation that was used in Section 7.2.

We note that the Planck mean is computed by omitting the scattering from the opacity and using the stimulated emission correction on the absorption part. It is possible (just for amusement, perhaps) to cancel the factor $1 - \exp(-h\nu/kT)$ in the corrected opacity with the similar factor in the denominator of the Planck function, and thereby calculate the numerator integral using the *uncorrected* absorption opacity and the Wien approximation $(2h\nu^3/c^2)\exp(-h\nu/kT)$ to the Planck function. This is to say that the emissivity does not care whether the photons are bosons or not.

Some general remarks on the two types of mean opacity are in order. When the spectral distribution of κ_ν is very complex, with a great many strong lines, photoionization edges, and so on, the dynamic range of κ_ν may be very large. In the center of a strong line we are not surprised to find opacity values of $10^{10}\,\mathrm{cm^2\,g^{-1}}$, while in the windows between lines, and below absorption edges, the opacity may become as low as the scattering part, which is around $0.2\,\mathrm{cm^2\,g^{-1}}$, giving a range of ten orders of magnitude! In this circumstance the Planck mean, since it is a linear mean, may be orders of magnitude larger than the Rosseland mean, which is like a harmonic, i.e., reciprocal, mean. In very tenuous plasmas the scattering can be much larger than the absorption opacity, with the result that the Rosseland mean, which includes scattering, can be much larger than the Planck mean, which does not. These gross variations should be kept in mind and appropriately applied to the problem at hand.

Another remark concerns the relative importance of different elements in a mixed plasma such as the astrophysical mixture, which has large amounts of H and He, and progressively smaller amounts of heavier elements C, N, O, Ne, Na, Mg, Al, Si, and on to Fe and Ni. The atomic fraction of Fe is only about 4×10^{-5} compared with H. Nonetheless, Fe is the dominant opacity contributor under some plasma conditions. The reason is that at high temperature all the lighter elements,

and abundant H and He in particular, are fully stripped: the mean number of bound electrons is quite small. This eliminates bound–bound and bound–free absorption for these elements. What is left is free–free absorption, which is relatively weak except at low frequency. The heavier elements still have several bound electrons under the same conditions, and therefore their opacity contribution is considerable. Even if Fe, say, were fully stripped its opacity contribution would be large in comparison to its abundance because of the Z^2 factor in (8.79); accounting for this factor we see that Fe free–free contributes 3% as much as H free–free.

The procedure for computing opacities runs like this. A theory of atomic structure is first used to determine the energy levels and ionization potentials of all the relevant ions of all the elements thought to make significant contributions to the total opacity, and, if necessary, the wave functions that go with each energy level. Then the oscillator strengths of all the possible transitions are computed from these wave functions, and the photoionization cross sections as well. If the atomic structure is being treated in a simplified way, then perhaps simple formulae or just the hydrogenic values may be used, thereby avoiding having to calculate large numbers of radial integrals by numerical quadrature. The photoionization cross sections and perhaps the free–free cross sections are found by other quadratures or other formulae.

The final step before the opacity can be computed is to determine the broadening of the spectral lines. The Doppler broadening is easy: a Gaussian distribution with a standard deviation $\Delta \nu = \nu \sqrt{kT/Mc^2}$, where M is the mass of the atom. Electron collisions, by themselves, generally make a Lorentzian profile $(\Gamma/4\pi^2)/[(\nu - \nu_0)^2 + (\Gamma/4\pi)^2]$, where Γ is the rate of electron collisions with the radiating atom. Ions in the plasma have a different effect: they do not move rapidly enough to interrupt the process of radiation, which is what leads to the Lorentzian profile. Instead, the radiation occurs while there is a reasonably constant configuration of perturbing ions. For each configuration there is a certain value of the electric field at the location of the radiating atom, which shifts the energy levels through the Stark effect. The probability distribution of the electric field (plasma microfield), folded with the relations that determine the level shifts in terms of the field, gives the line broadening contribution due to ions. (In more sophisticated calculations the ions are not treated as completely stationary, nor are the electrons treated with a simple Lorentzian profile.) The Doppler broadening, electron impact broadening, and ion broadening are the major mechanisms, but other mechanisms must be included in special cases.

The calculation of opacities for astrophysical use has evolved greatly over the years, as we might have expected. The first calculations applied the hydrogenic formulae to all elements, and in fact omitted the line contribution entirely. Such were the opacity calculations by Keller and Meyerott (1955), for example. (Although

some elements were represented using Hartree-type wave functions.) In the next generation, the Cox and Stewart opacities of the 1960s (Cox, Stewart, and Eilers, 1965, Cox and Stewart, 1965), the hydrogenic formulae were still used, but with scaling factors to account for the shielding of the nucleus by other electrons in a multielectron ion. The line absorption was included for the first time. At around the same time the Thomas–Fermi method was developed as an alternative to the hydrogenic model. In this approach single-electron wave functions were actually computed numerically using for the central potential the solution of the Thomas–Fermi model atom. For technical reasons this approach gave opacities similar in accuracy to the scaled hydrogenic method. The advances in opacity theory since the 1970s have included using the Hartree–Fock self-consistent field method to get much more accurate values of the energy levels and the wave functions. (The Fock part of the name means that antisymmetry of the wave functions was explicitly built in, by using both a direct and an exchange part of the electron–electron potential function.) It should be noted that even the very best of these atomic structure calculations is far less accurate than the experimental determinations of atomic energy levels. One might ask: why not just use the experimental data? The problem is that the experimental data are not complete enough to supply all the levels that are needed, and the energy level information does not help much with determining the oscillator strengths and cross sections. A saving fact is that the mean opacity is really not very sensitive to the precise values of the transition frequencies. If the calculated frequencies are statistically correct then the opacity will be about right, when the average is taken, even though some of the lines have been shifted around compared with the true frequencies. There have been advances beyond Hartree–Fock as well. Some opacity calculations (e.g., the Opacity Project (Seaton, 1995)) have used the method of configuration interaction, in which the multielectron Hamiltonian is computed for a large basis set of somewhat arbitrarily selected states, then diagonalized to determine energy levels and eigenfunctions. This method can be very accurate provided the basis set is large enough.

So far the methods described have treated the atoms as isolated entities, so the wave functions are calculated as extending to $r = \infty$. This is a reasonable approximation when the mean distance between ions is much larger than the radius of the Bohr orbits of interest, which is about $n^2 a_0/Z^*$ in terms of the principal quantum number n and the ion charge Z^*. It is not a good approximation when the mean ion spacing is small, nor is it a good model for highly excited states. Calculating the atomic states and their occupation probabilities for dense plasmas is a significant challenge. The OPAL opacity code uses a less elaborate atomic structure method than the configuration-interaction method adopted for the Opacity Project – OPAL uses the parametric-potential method, a fitting technique – but applies quite
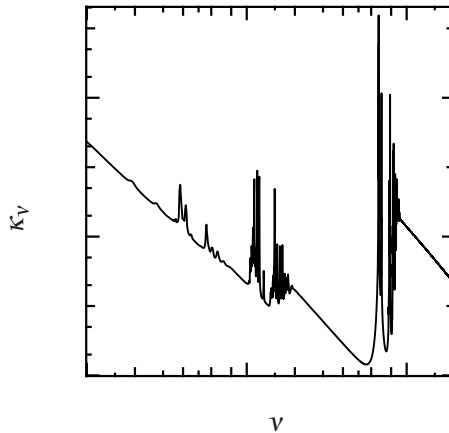
Fig. 8.2 The monochromatic opacity of iron calculated with OPAL is shown for the conditions $T = 1\,\text{keV}$, $\rho = 1\,\text{g\,cm}^{-3}$.

a sophisticated treatment of the electron–electron, electron–ion and ion–ion correlations that arise because the charges are close enough to interact strongly. OPAL calculates all the individual lines from the various configurations in detail, including the relativistic fine structure, and uses a careful treatment of ion microfield broadening and electron impact broadening. Thus even though the individual line frequencies are not given to high accuracy by the parameterized-potential method, the OPAL opacities have been shown to be free from major systematic errors. A sample OPAL opacity calculation for iron is shown in Figure 8.2 and illustrates the universal properties of a general ν^{-3} dependence of the bound–free and free–free opacity between edges and lines, the high value attained by the free–free opacity at low ν, the jumps at bound–free edges that are ever-larger as ν increases until the last one (the K edge) is reached, and the extremely large values of opacity attained within the lines, which tend to cluster on the low-ν side of the edges. This example is neither unusually simple nor unusually complex in terms of line structure.

The OPAL and Opacity Project opacity databases are nicely reviewed in Seaton (1995), Berrington (1995), and Rogers and Iglesias (1995). The opacity project is also described by Seaton, Yu, Mihalas, and Pradhan (1994), and the latest OPAL results by Iglesias and Rogers (1996).

An approach such as that used in OPAL and in the Opacity Project, in which every line is computed individually to form a spectrum, fails badly when there are atomic shells, perhaps several of them, that contain several electrons with larger angular momenta, such as $3d^{6}4s4p^{3}$, for example. Some success has been achieved in these complicated atoms by using the ideas of unresolved transition arrays (UTAs) and super transition arrays (STAs). Using powerful modern methods

for angular momentum algebra, Bauche, Klapisch and others (see Bauche and Bauche-Arnoult (1990)) have found formulae for the mean and standard deviation of the line frequencies connecting two whole configurations or even small sets of configurations, and their statistically-based calculations of the spectrum give an acceptably accurate result in some otherwise intractable cases.

It must be clear that the calculation of opacity has become much more elaborate than in the days of Keller and Meyerott, when a simple subroutine could compute the opacity quickly and easily just when it was needed. The present-day elaborate opacity calculations take an hour or more of computer time just to find the opacity at a single temperature–density point. The only way to use such opacities that makes practical sense is as tables that are read into memory and that are used to supply values by interpolation when they are needed. Indeed, the use of larger and larger tables of opacity has been common since the production of the Los Alamos Opacity Library in the 1970s (Huebner, Merts, Magee, and Argo, 1977). In some of today's advanced stellar atmosphere modeling the frequency-dependent opacity is needed as well as, or instead of, the Rosseland mean, and these tables are now saved when the opacity codes are run. The size of these tables is very large, but, as we will see shortly, all the other aspects of the radiation hydrodynamic calculations that use multifrequency opacities are large as well.