RAYLEIGH AND RAMAN SCATTERING

9.1. Introduction

The statistical multi-level approach of the preceding chapter that is based on the density matrix formalism provides a foundation for physical understanding and for the treatment of quite general problems. It can account for the effects of coherences of any atomic level, although the effects of collisions are included in a phenomenological and incomplete way (this will be improved on in the next chapter). In practice, however, coherence phenomena play a significant role only in connection with scattering processes (Rayleigh, resonant, Raman, and fluorescent scattering). The dominant polarization effects come from the coherences in the intermediate, excited states of the scattering process, while lower-state coherences only result in minor perturbations of the scattering polarization, effects that would be very hard to measure in astrophysical situations. It is therefore a good approximation to neglect atomic polarization and coherences (phase relations between the magnetic substates) of the initial level of the scattering process. This greatly simplifies the problem, since the scattering polarization may be calculated without solving the polarized statistical equilibrium equations.

The reason why initial-level coherences are expected to be small is that the lower level is generally long-lived so that the magnetic substates become well separated even for very weak fields (which are present everywhere in the solar atmosphere), and that the rate of collisions, which scramble the relative phases, is generally much higher than the inverse life-time of the initial atomic state, at least in the part of the solar atmosphere where most of the spectral lines in the visible part of the solar spectrum are formed.

Instead of using the cumbersome general formalism it is for the above reasons preferable to develop a special scattering formalism, which is much simpler and more transparent, and with which closed analytical expressions can be developed. In most cases this is the only formalism that needs to be used for treating coherence effects in the solar atmosphere, without having to resort to the general theory. In the end of the previous chapter we indicated how the scattering processes could be formulated in terms of a scattering phase matrix $\boldsymbol{P}$, which constitutes the connection between the quantum field theory and the classical treatment of Chapter 5. As we will show below, $\boldsymbol{P}$ always has the form given by Eq. (5.68), regardless of whether we are dealing with Rayleigh or Raman scattering, as long as we neglect coherences and atomic polarization in the initial atomic state. The physics of coherence phenomena on the sun (in the rest frame, excluding collisional effects) then boils down to the calculation of the expressions for the polarizability factors $W_{1,2}$ in the phase matrix of Eq. (5.68).

The physics of scattering may be treated in a unified way, to cover the various cases that can occur. The two main categories of scattering processes are *Rayleigh* and *Raman* scattering. In our terminology Rayleigh scattering refers to the case when the n, L, and J quantum numbers are the same for the initial and final states of the scattering process, Raman scattering to the case when any one of these numbers is different. In the special case of Rayleigh scattering when the incident photon has a frequency that differs from the resonant frequency of an atomic transition by an amount that is not much larger than the natural damping width of the transition one usually speaks of *resonant* scattering. The corresponding special case of Raman scattering is called *fluorescent* scattering. For Rayleigh and Raman scattering in the distant dispersion wings of a transition the scattering is frequency coherent as a consequence of energy conservation, but for resonant and fluorescent scattering one has to deal with the more complex partial redistribution problem (see next chapter).

After we have explored the symmetry properties of the phase matrix we will derive algebraic expressions for the polarizabilities $W_{1,2}$ in terms of the L, S, and J quantum numbers, for both Rayleigh and Raman scattering, including the case when there are arbitrary quantum-mechanical interferences in the excited state between levels with different total angular momentum quantum numbers J_m. These expressions are then checked by invoking a generalized principle of spectroscopic stability (requiring that the expressions should become independent of the spin quantum number S when the fine-structure splitting goes to zero).

One aspect that has not been accounted for by the statistical formalism of the preceding chapter is the frequency correlation between the absorption and scattering events. As the frequency redistribution was given in terms of a profile function Φ and the individual transitions in the statistical equilibrium were treated as stochastically independent of each other, the special case of complete frequency redistribution (cf. Chapter 5) was implicitly assumed. The most direct avenue of making frequency coherence between absorption and scattering manifest and to obtain the rest frame scattering redistribution matrix is via time-dependent quantum-mechanical perturbation theory, which we will introduce in the next section (in the absence of collisions and atomic polarization of the initial atomic state).

9.2. Transition Rates in Time-dependent Perturbation Theory

If the initial state (at time $t = 0$) of the atom is the eigenstate $|\,a\,\rangle$, then the solution (7.2) of the Schrödinger equation (7.1) for the wave function at time t is given by

$$\psi(t) = e^{-i\hat{H}t/\hbar}\,|\,a\,\rangle. \tag{9.1}$$

The probability of finding the system at time t in the final state $|\,f\,\rangle$ is

$$|\,\langle\,f\,|\,\psi(t)\,\rangle\,|^2 = |\,\langle\,f\,|\,e^{-i\hat{H}t/\hbar}\,|\,a\,\rangle\,|^2. \tag{9.2}$$

The transition rate $1/\tau$ per atom for transitions from state $|\,a\,\rangle$ to all possible states $|\,f\,\rangle$ is

$$\frac{1}{\tau} = \frac{\mathrm{d}}{\mathrm{d}t} \sum_f |\langle f \,|\, \psi(t) \,\rangle|^2 , \tag{9.3}$$

where we have summed over all the final substates. As we will see, Eq. (9.3) gives us to first order of the perturbation (of the Hamiltonian $\hat{H}$) the Einstein A_{ji} or B_{ij} coefficients, to second order the Kramers-Heisenberg scattering cross section.

According to Eq. (7.12) we can write $\hat{H}$ as a sum of a time-independent part $\hat{H}_0$ and a time-dependent perturbation $\hat{H}'$. Only the latter is capable of changing the state of the system. Since $\hat{H}_0$ and $\hat{H}'$ do not commute, we cannot expand the exponential $\exp(-i\hat{H}t/\hbar)$ in the normal, straightforward way, but with some mathematical transformations a perturbation expansion is still possible. We will here not list these mathematical steps, since they are part of standard time-dependent perturbation theory (cf. Loudon, 1983), but instead give the results for τ to second order in the perturbation $\hat{H}'$:

$$\frac{1}{\tau} \approx \frac{2\pi}{\hbar^2} \sum_f \left| \langle f \,|\, \hat{H}' \,|\, a \,\rangle \right.$$
$$\left. + \sum_b \frac{\langle f \,|\, \hat{H}' \,|\, b \,\rangle \langle b \,|\, \hat{H}' \,|\, a \,\rangle}{E_a - E_b} \right|^2 \delta\left(\frac{E_a - E_f}{\hbar}\right) . \tag{9.4}$$

It is important to remember that the energies $E_{a,b,f}$ involved here represent matter *and* radiation together, not just the atomic system. When the atomic parts of a and f are different, a photon exchange is therefore necessary to make the δ function, which represents energy conservation, different from zero. The first term on the right-hand side of Eq. (9.4) contains $\hat{H}'$ only once (first-order contribution) and consequently represents the transition rate with the exchange of a single photon. The second term, where $\hat{H}'$ occurs twice (second-order contribution), represents a two-photon process with an intermediate state b, i.e., a scattering event.

9.3. Explicit Expressions for the Transition Rates

To explicitly evaluate Eq. (9.4) we can use expressions (7.63) and (7.64) for $\hat{H}'$ and as in Sect. 8.4 calculate all the proportionality factors and integrate over all the photon states. For the first-order contribution to Eq. (9.4) we then obtain

$$\left(\frac{1}{\tau}\right)_{\text{first order}} = \frac{2\pi}{\hbar^2} \sum_f \left| \langle f \,|\, \hat{H}' \,|\, a \,\rangle \right|^2 \delta\left(\frac{E_a - E_f}{\hbar}\right) = \sum_f A_{af} , \tag{9.5}$$

where A_{af} is the Einstein coefficient of spontaneous emission if we assume that the atomic state $|\, a \,\rangle$ is above the $|\, f \,\rangle$ state.

The second-order contribution that represents scattering involves two photons, the incident one with frequency ω', and the scattered one with frequency ω. If we denote the atomic frequencies of the initial and final states by ω_a and ω_f, we have

$$E_a = \hbar(\omega' + \omega_a)\,,$$
$$E_f = \hbar(\omega + \omega_f)\,. \tag{9.6}$$

The scattering transition rate then becomes

$$\left(\frac{1}{\tau}\right)_{\text{scattering}} = \frac{2\pi}{\hbar^2} \sum_{f_{\text{atom}}} \sum_{\boldsymbol{k}} |w|^2 \, \delta(\omega' - \omega + \omega_a - \omega_f)\,, \tag{9.7}$$

where

$$w = \frac{1}{\hbar} \sum_b \frac{\langle f | \hat{H}' | b \rangle \langle b | \hat{H}' | a \rangle}{\omega' + \omega_a - E_b/\hbar}\,. \tag{9.8}$$

It follows from Eq. (7.44) that $\sum_{\boldsymbol{k}}$ can be replaced by a factor that is proportional to ω^2, and which also involves a frequency integration. We then get for the differential scattering cross section $\mathrm{d}\sigma$ per unit solid angle and unit frequency interval

$$\mathrm{d}\sigma \sim \sum_{f_{\text{atom}}} \omega^2 \, |w|^2\,. \tag{9.9}$$

The δ function of Eq. (9.7) is not present in Eq. (9.9), since it disappeared when making the frequency integration of $\sum_{\boldsymbol{k}}$.

Since $\hat{H}'$ appears twice in Eq. (9.8), the scattering amplitude w will contain bilinear combinations of creation and annihilation operators, as follows from Eq. (7.63). As the photon number is conserved in the scattering process, the bilinear combinations have to contain one each of the creation and annihilation operators, but not two of the same kind. The order in which the two operators occur determines the nature of the physical process as well as the value of E_b. Figure 9.1 gives a graphical illustration of the two basic contributions to the scattering amplitude.

The upper diagram of Fig. 9.1 represents the resonant process of absorption followed by emission. At the right vertex a photon with wave number vector $\boldsymbol{k}'$ is destroyed (operator $\hat{a}_{\boldsymbol{k}'}$), and the atomic state a is destroyed (operator $\langle a |$), while the atomic state b is created (operator $| b \rangle$). At the left vertex a photon with wave number vector $\boldsymbol{k}$ is created (operator $\hat{a}_{\boldsymbol{k}}^\dagger$), atomic state b is destroyed (operator $\langle b |$), while atomic state f is created (operator $| f \rangle$). In Eq. (9.8) this means that the surviving contribution of $\hat{H}'$ to the right matrix element of w has the form $| b \rangle \langle a | \hat{a}_{\boldsymbol{k}'}$, while for the left matrix element the contribution is $| f \rangle \langle b | \hat{a}_{\boldsymbol{k}}^\dagger$. In this case the intermediate state contains only an atomic but no photon contribution, which means that $E_b = \hbar\omega_b$. Then the denominator in Eq. (9.8) is $\omega' + \omega_a - E_b/\hbar = \omega' - \omega_{ba}$, where by definition $\omega_{ba} = \omega_b - \omega_a$. Since the energy conservation dictated by the δ function in Eq. (9.7) implies that

$$\omega' - \omega + \omega_{af} = 0\,, \tag{9.10}$$

the denominator of the resonant term becomes

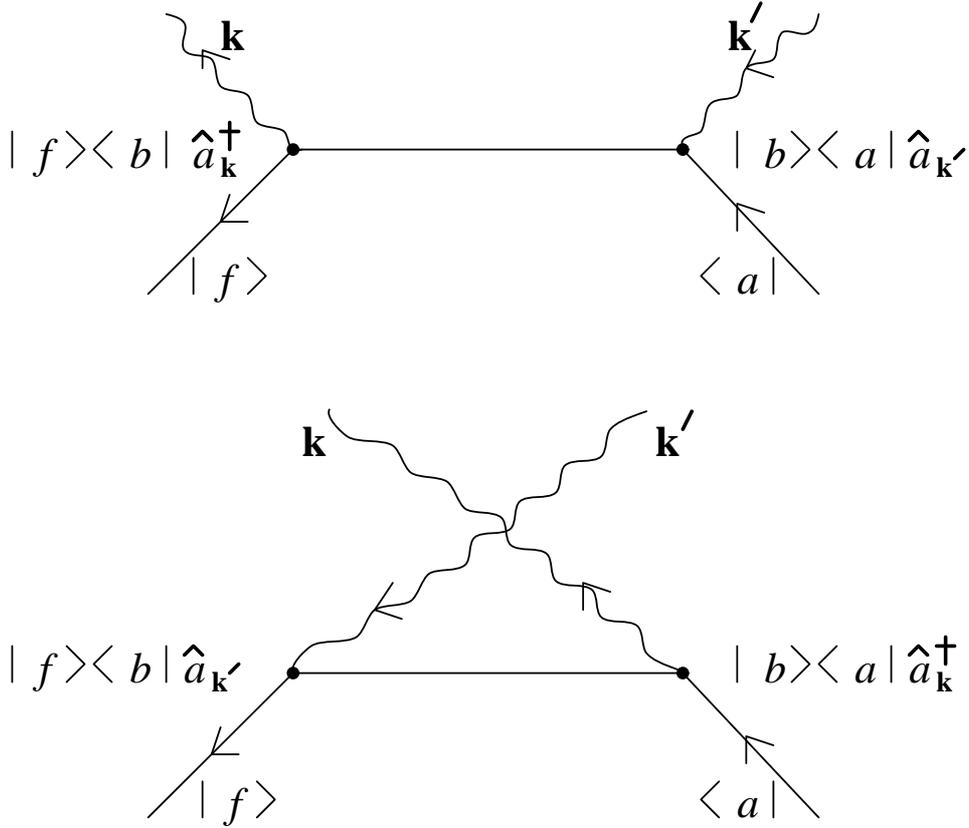$$\omega' - \omega_{ba} = \omega - \omega_{bf}\,. \tag{9.11}$$

Fig. 9.1. Illustration of the two contributions to the scattering amplitude w (see text).

The lower diagram of Fig. 9.1 differs from the upper one only in the ordering of the creation and annihilation operators. This implies reversal of the time ordering, so that the diagram represents the non-resonant process of emission followed by absorption. In this case the intermediate state contains *two* photons, so that

$$E_b/\hbar = \omega_b + \omega' + \omega\,. \tag{9.12}$$

The denominator of the non-resonant term then becomes

$$\omega' + \omega_a - E_b/\hbar = -(\omega + \omega_{ba})\,. \tag{9.13}$$

Combining these results and using Eq. (7.63) where the coefficients $d_{j\ell\mathbf{k}}$ were introduced, Eq. (9.8) for the scattering amplitude can be written

$$w = \frac{1}{\hbar} \sum_b \left\{ \frac{d^\dagger_{fb\mathbf{k}}\, d_{ba\mathbf{k}'}}{\omega - \omega_{bf}} - \frac{d_{fb\mathbf{k}'}\, d^\dagger_{ba\mathbf{k}}}{\omega + \omega_{ba}} \right\}. \tag{9.14}$$

The non-resonant term is almost never of practical importance, so we will disregard it in the following. For the resonant term our simplified second-order treatment leads to an undamped singularity at the resonant frequency, but because the lifetime of the intermediate state is finite, damping will of course always be

present. As in the previous chapters we introduce damping heuristically, and refer to the discussion and arguments of Sects. 7.9, 8.5, and 10.1. Further, as ω^2 in Eq. (9.9) is $\approx \omega_{bf}^2$, it can usually be regarded as a fixed constant of proportionality for the scattering cross section. For the time being we will omit the proportionality constant but reclaim it again in Sect. 9.14, where we will give the expression for the absolute magnitude of the scattering cross section.

Using expressions (7.64) for $d_{j\ell \boldsymbol{k}}$ and letting the indices $\boldsymbol{k}$ and $\boldsymbol{k}'$ be represented by the photon polarization indices α and β as we did in the previous two chapters, we obtain for the scattering amplitude $w = w_{\alpha\beta}$:

$$w_{\alpha\beta} \sim \sum_b \frac{\langle\, f \,|\, \hat{\boldsymbol{r}} \cdot \boldsymbol{e}_\alpha \,|\, b \,\rangle \langle\, b \,|\, \hat{\boldsymbol{r}} \cdot \boldsymbol{e}_\beta \,|\, a \,\rangle}{\omega_{bf} - \omega - i\gamma/2}\,. \tag{9.15}$$

Since $w_{\alpha\beta}$ is a tensor and not a scalar, and since the general polarization states of the incident and scattered photons are mixed states involving products of creation and annihilation operators representing different polarization states, as shown by the radiation coherency matrix (7.53), we need to generalize the expression for the differential scattering cross section $d\sigma$ such that $|w|^2 = ww^*$ is replaced by the tensor product $\boldsymbol{w} \otimes \boldsymbol{w}^*$ as in Eq. (8.114). We thus get

$$d\sigma \sim \sum_{f_{\text{atom}}} \boldsymbol{w} \otimes \boldsymbol{w}^*\,, \tag{9.16}$$

where we have summed over all the final atomic substates. This expression is identical to that for the $\boldsymbol{W}$ matrix in Eq. (8.114), since we have implicitly assumed that we have complete redistribution in the initial state (the diagonal density matrix elements $\rho_{\mu_i \mu_i}$ are independent of μ_i), and the summation label μ_f corresponds to our summation label f_{atom}.

9.4. Symmetry Properties of the Phase Matrix

The matrix $\boldsymbol{W} = \boldsymbol{w} \otimes \boldsymbol{w}^*$ describes scattering of the radiation coherency matrix. In a Stokes vector formalism the counterpart is the phase matrix $\boldsymbol{P} \sim \boldsymbol{T}\boldsymbol{W}\boldsymbol{T}^{-1}$, as shown by Eq. (2.48) and in Sects. 5.9, 5.10, and 8.10. In Eq. (5.68) we extended the classical expression for $\boldsymbol{P}$ to the general quantum-mechanical case by introducing the coefficients W_1 and W_2, but did not show how this expression was obtained or that such a symmetry property of $\boldsymbol{P}$ at all applies to all the various scattering cases (including Raman scattering) that can occur. This demonstration will now be done.

The factors W_1 and W_2 enter naturally in our present theoretical framework, and we are in a position to derive explicit expressions for them in terms of the quantum numbers of the transitions. W_1 is a scaling factor for the scattering cross section for circular polarization (Stokes V), which equals unity in the classical case, whereas W_2 represents the fraction of the scattering processes that affect the linear polarization in the same way as classical dipole scattering. The fraction $1 - W_2$ represents isotropic, unpolarized scattering. Note that the parameters $W_{1,2}$ should

not be confused with the elements W_{ij} of the $\boldsymbol{W}$ matrix. The notation happens to be similar due to the limited choice offered by the alphabet.

Before proving the symmetry properties of $\boldsymbol{P}$ represented by Eq. (5.68), we rewrite this equation into a form that will be more useful here. In the limit of vanishing magnetic field we obtain from Eqs. (5.68) and (5.58)–(5.64) for the special case when the scattering angles $\theta' = \theta = \pi/2$ (i.e., when the scattering takes place in the equatorial plane, cf. Fig. 3.3)

$$\boldsymbol{P} = \boldsymbol{E}_{11} + \tfrac{3}{4}W_2(\boldsymbol{P}_0^2 + \boldsymbol{P}_2^2\cos 2\phi)$$
$$+ \tfrac{3}{2}(W_2\boldsymbol{E}_{33} + W_1\boldsymbol{E}_{44})\cos\phi \tag{9.17}$$

with

$$\boldsymbol{P}_0^2 = \frac{1}{2}\begin{pmatrix} \tfrac{1}{3} & 1 & 0 & 0 \\ 1 & 3 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix},$$
$$\boldsymbol{P}_2^2 = \frac{1}{2}\begin{pmatrix} 1 & -1 & 0 & 0 \\ -1 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}. \tag{9.18}$$

$\boldsymbol{E}_{jj}$ is a matrix that has its diagonal element at position jj equal to unity, while all the remaining elements are zero. Inserting the expressions of Eq. (9.18) in Eq. (9.17), we get

$$\boldsymbol{P} = W_2\boldsymbol{P}_R + (1 - W_2)\boldsymbol{E}_{11} + W_1\boldsymbol{E}_{44}\tfrac{3}{2}\cos\phi, \tag{9.19}$$

where

$$\boldsymbol{P}_R = \frac{3}{4}\begin{pmatrix} 1 + \cos^2\phi & \sin^2\phi & 0 & 0 \\ \sin^2\phi & 1 + \cos^2\phi & 0 & 0 \\ 0 & 0 & 2\cos\phi & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \tag{9.20}$$

represents the classical dipole-type Rayleigh scattering matrix for the linear polarization. The second term on the right hand side of Eq. (9.19) represents isotropic, unpolarized scattering, the third term refers only to scattering of Stokes V (which is decoupled from the other Stokes parameters in the scattering process), while the first term represents dipole-type scattering scaled by the factor W_2.

When trying to reproduce the form represented by Eq. (9.19) from quantum mechanics, it is natural to start by exploring the symmetry properties of the matrix $\boldsymbol{W}$, whose elements are governed by the geometrical ε factors and the 3-j symbols according to Eqs. (8.115) and (8.117) when lower-state coherences are disregarded. These symmetry properties are found most easily with the coordinate system of Fig. 3.3, which was used for Eqs. (9.17)–(9.20). Thus we assume that the incident radiation is travelling along the x-axis, the scattering takes place in the xy plane, and the scattering angle is ϕ. Let us further mark incident polarization states with a prime, which means that index β of Eq. (9.15) should be replaced by $1'$ or $2'$, while $\alpha = 1$ or 2. With our choice of scattering geometry it follows from Eq. (3.86) that

$$\varepsilon_0^1 = \varepsilon_0^{1'} = -1\,,$$
$$\varepsilon_0^2 = \varepsilon_0^{2'} = \varepsilon_\pm^1 = \varepsilon_\pm^{1'} = 0\,,$$
$$\varepsilon_\pm^2 = -i\,e^{\pm i\phi}/\sqrt{2}\,,$$
$$\varepsilon_\pm^{2'} = -i/\sqrt{2}\,.$$

(9.21)

In the following we will consider the general case of Raman scattering, which includes Rayleigh scattering as the special case when the initial and final states are the same. Inserting Eq. (9.21) in Eq. (8.117) and using Eq. (2.39), we find that

$$W_{12} = W_{21} = W_{13} = W_{31} = W_{24} = W_{42} = W_{34} = W_{43} = 0\,,$$
$$W_{22} = W_{33}\,,$$
$$W_{23} = W_{32}\,,$$
$$W_{14} = W_{41}\,.$$

(9.22)

The validity of these relations is readily seen by direct inspection of the expressions for the different elements, except for the last relation, $W_{14} = W_{41}$, which is not so obvious in the Raman scattering case, when $J_{\mu_i} \neq J_{\mu_f}$ (see the explicit expression for W_{14} below). It can be shown, however, that this symmetry property like all the other relations in Eq. (9.22) is valid for all Raman scattering cases.

As a consequence of Eq. (9.22) $\boldsymbol{W}$ has the form

$$\boldsymbol{W} = \begin{pmatrix} W_{11} & 0 & 0 & W_{14} \\ 0 & W_{22} & W_{23} & 0 \\ 0 & W_{23} & W_{22} & 0 \\ W_{14} & 0 & 0 & W_{44} \end{pmatrix}.$$

(9.23)

It follows that the phase matrix $\boldsymbol{P}$ can be written as

$$\boldsymbol{P} \sim \boldsymbol{TWT}^{-1} = \frac{1}{2}\begin{pmatrix} a & b & 0 & 0 \\ b & c & 0 & 0 \\ 0 & 0 & d & 0 \\ 0 & 0 & 0 & e \end{pmatrix},$$

(9.24)

where

$$a = W_{11} + 2W_{14} + W_{44}\,,$$
$$b = W_{11} - W_{44}\,,$$
$$c = W_{11} - 2W_{14} + W_{44}\,,$$
$$d = 2(W_{22} + W_{23})\,,$$
$$e = 2(W_{22} - W_{23})\,.$$

(9.25)

Next we will write down the explicit expressions for the non-zero elements of the $\boldsymbol{W}$ matrix and show how the phase matrix $\boldsymbol{P}$ in Eq. (9.24) can be brought to a form that is identical to that of Eq. (9.19). As a byproduct we will obtain the algebraic expressions for the polarizability coefficients $W_{1,2}$ in terms of the J_μ and J_m quantum numbers.

The derivation will first be made for the case when there is only one upper-level quantum number J_m, since then $W_{1,2}$ turn out to be well-defined constants, expressible in terms of J_m and J_μ only. When there are interferences between states of different total angular momentum J_m, one cannot factorize out the profile function Φ in Eq. (8.115) to form a frequency-independent phase matrix, unless the differences between the resonant frequencies of the different profile functions are small in comparison with the Doppler width. The resulting frequency dependence of the phase matrix can however be described using the algebraic expressions for $W_{1,2}$ for the individual levels as parameters of the frequency-dependent function (cf. Stenflo, 1980), as will be shown below in Sects. 9.8, 9.9, and 9.12.

From Eqs. (8.114), (8.117), and (9.21) we obtain in the case of complete redistribution for the lower level (when $\rho_{\mu_i \mu_i}$ is independent of μ_i)

$$
\begin{aligned}
W_{11} &\sim \sum_k \begin{pmatrix} J_m & J_{\mu_f} & 1 \\ -k & k & 0 \end{pmatrix}^2 \begin{pmatrix} J_m & J_{\mu_i} & 1 \\ -k & k & 0 \end{pmatrix}^2 , \\
W_{14} &\sim \sum_k \begin{pmatrix} J_m & J_{\mu_f} & 1 \\ -k & k & 0 \end{pmatrix}^2 \begin{pmatrix} J_m & J_{\mu_i} & 1 \\ -k & k-1 & 1 \end{pmatrix}^2 .
\end{aligned} \tag{9.26}
$$

The summation over k arises from the summation in Eq. (8.114) over μ_i and μ_f.

If J_{μ_f} and J_{μ_i} in W_{14} are exchanged, we obtain W_{41}. Although the equivalence of the expressions for W_{14} and W_{41} may not be obvious when $J_{\mu_f} \neq J_{\mu_i}$, it can be shown that they are the same.

In all our expressions for the matrix elements W_{ij} the not explicitly given proportionality constant contains the product $f_{J_{\mu_i} J_m} f_{J_{\mu_f} J_m}$ between the two oscillator strengths. When we later allow for interference between the different intermediate J_m states, the situation gets more complex, since we have to deal with products of $\pm \sqrt{f_{J_{\mu_{i,f}} J_m}}$, where the sign is determined in a fairly complicated way by the L, S, and J quantum numbers involved. We will treat this interference case in Sects. 9.7, 9.9, and 9.11 below.

Like Eqs. (9.26) we obtain

$$
\begin{aligned}
W_{22} &= W'_{22} \cos \phi , \\
W_{23} &= W'_{23} \cos \phi ,
\end{aligned} \tag{9.27}
$$

where

$$
\begin{aligned}
W'_{22} &\sim \sum_k \begin{pmatrix} J_m & J_{\mu_f} & 1 \\ -k & k & 0 \end{pmatrix} \begin{pmatrix} J_m & J_{\mu_i} & 1 \\ -k & k & 0 \end{pmatrix} \\
&\qquad \begin{pmatrix} J_m & J_{\mu_f} & 1 \\ -k-1 & k & 1 \end{pmatrix} \begin{pmatrix} J_m & J_{\mu_i} & 1 \\ -k-1 & k & 1 \end{pmatrix} , \\
W'_{23} &\sim -\sum_k \begin{pmatrix} J_m & J_{\mu_f} & 1 \\ -k & k & 0 \end{pmatrix} \begin{pmatrix} J_m & J_{\mu_i} & 1 \\ -k+1 & k-1 & 0 \end{pmatrix} \\
&\qquad \begin{pmatrix} J_m & J_{\mu_f} & 1 \\ -k+1 & k & -1 \end{pmatrix} \begin{pmatrix} J_m & J_{\mu_i} & 1 \\ -k & k-1 & 1 \end{pmatrix} .
\end{aligned} \tag{9.28}
$$

The following two relations can also be derived from the properties of the 3-j symbols:

$$W'_{22} + W'_{23} = W_{11} - W_{14} \,,$$
$$W_{44} - W_{14} = (W_{11} - W_{14}) \cos^2 \phi \,.$$
$$(9.29)$$

Using relations (9.27) and (9.29) in Eq. (9.25), we now obtain

$$a = (W_{11} - W_{14})(1 + \cos^2 \phi) + 4W_{14} \,,$$
$$b = (W_{11} - W_{14}) \sin^2 \phi \,,$$
$$c = (W_{11} - W_{14})(1 + \cos^2 \phi) \,,$$
$$d = 2(W_{11} - W_{14}) \cos \phi \,,$$
$$e = 2(W'_{22} - W'_{23}) \cos \phi \,.$$
$$(9.30)$$

Comparison between Eq. (9.24) with expressions (9.30) inserted and Eq. (9.19) shows that the two expressions for the phase matrix become identical if the parameters $W_{1,2}$ satisfy the relations

$$\tfrac{3}{4}W_2 + (1 - W_2) = k(W_{11} + 3W_{14}) \,,$$
$$\tfrac{3}{4}W_2 = k(W_{11} - W_{14}) \,,$$
$$\tfrac{3}{4}W_1 = k(W'_{22} - W'_{23}) \,,$$
$$(9.31)$$

where k is a proportionality (or normalization) constant. The solution of Eqs. (9.31) is

$$W_1 = \frac{W'_{22} - W'_{23}}{W_{11} + 2W_{14}} \,,$$
$$W_2 = \frac{W_{11} - W_{14}}{W_{11} + 2W_{14}} \,.$$
$$(9.32)$$

9.5. Expressions for $W_{1,2}$

When Eqs. (9.26) and (9.28) are inserted in Eqs. (9.32), it is possible to compute the values of $W_{1,2}$ for any combination of the J_m, J_{μ_i}, and J_{μ_f} quantum numbers. It is however not necessary to evaluate the sums over the 3-j symbols each time, since simple algebraic expressions for these sums in terms of J_m, J_{μ_i}, and J_{μ_f} can be derived and used, as will be seen below.

The most compact way of writing the solutions for W_K, $K = 1, 2$, has been given by Landi Degl'Innocenti (1984):

$$W_K = w^{(K)}_{J_m J_{\mu_i}} \, w^{(K)}_{J_m J_{\mu_f}} \,,$$
$$(9.33)$$

where $w^{(K)}_{J_m J_\mu}$ should not be confused with the scattering amplitudes $w_{\alpha\beta}$. Instead they are algebraic expressions in terms of 6-j symbols:

$$w_{J_m J_\mu}^{(K)} = \left\{ \begin{matrix} 1 & 1 & K \\ J_m & J_m & J_\mu \end{matrix} \right\} \Bigg/ \left\{ \begin{matrix} 1 & 1 & 0 \\ J_m & J_m & J_\mu \end{matrix} \right\} . \tag{9.34}$$

As the general algebraic expression for 6-j symbols is not so transparent, and as all the various scattering possibilities can be represented by a small number of cases corresponding to different possible combinations of J quantum numbers, it is much more convenient to write down and work with the explicit solutions for these possible cases. These solutions will now be listed in the form of simple algebraic expressions.

In the Rayleigh scattering case, when $J_{\mu_f} = J_{\mu_i} = J_\mu$, only the three cases when $J_m - J_\mu = 0, \pm 1$ can occur (but $J_m = J_\mu = 0$ is forbidden). The simple and compact algebraic expressions for these three cases have previously been given by Chandrasekhar (1950). We list them in the order of increasing value of J_m (for a given value of J_μ).

CASE I. $J_m = J_\mu - 1 = J - 1$

$$\begin{aligned} W_1 &= \frac{J-1}{2J} , \\ W_2 &= \frac{(J-1)(2J-3)}{10J(2J+1)} . \end{aligned} \tag{9.35}$$

CASE II. $J_m = J_\mu = J$

$$\begin{aligned} W_1 &= \frac{1}{2J(J+1)} , \\ W_2 &= \frac{(2J-1)(2J+3)}{10J(J+1)} . \end{aligned} \tag{9.36}$$

CASE III. $J_m = J_\mu + 1 = J + 1$

$$\begin{aligned} W_1 &= \frac{J+2}{2(J+1)} , \\ W_2 &= \frac{(J+2)(2J+5)}{10(J+1)(2J+1)} . \end{aligned} \tag{9.37}$$

Note that Cases I–III also apply to the case of Raman scattering when $J_{\mu_f} = J_{\mu_i}$ while $L_f \neq L_i$.

The symmetry of W_K with respect to an exchange of J_{μ_f} and J_{μ_i}, e.g. as shown by Eq. (9.33), implies invariance of W_K with respect to reversal of the order of the scattering (time reversal). This reduces the number of additional cases to be listed to three, to fully cover all the Raman scattering cases that can occur. We have used the explicit algebraic expressions for the 3-j symbols in Eqs. (9.26) and (9.28) to derive simple algebraic expressions for these additional cases, analogous to the

Chandrasekhar expressions for the Rayleigh scattering case. These solutions will now be listed. In Cases IV and V $J_{\mu_f} - J_{\mu_i} = 1$ (the two cases are listed in the order of increasing value of J_m for fixed values of J_{μ_f} and J_{μ_i}), in Case VI $J_{\mu_f} - J_{\mu_i} = 2$.

CASE IV. $J_m = J_{\mu_f} - 1 = J_{\mu_i} = J$

$$
\begin{aligned}
W_1 &= -\frac{1}{2(J+1)}, \\
W_2 &= -\frac{2J-1}{10(J+1)}.
\end{aligned}
\tag{9.38}
$$

CASE V. $J_m = J_{\mu_f} = J_{\mu_i} + 1 = J + 1$

$$
\begin{aligned}
W_1 &= \frac{1}{2(J+1)}, \\
W_2 &= -\frac{2J+5}{10(J+1)}.
\end{aligned}
\tag{9.39}
$$

CASE VI. $J_m = J_{\mu_f} - 1 = J_{\mu_i} + 1$

$$
\begin{aligned}
W_1 &= -\frac{1}{2}, \\
W_2 &= \frac{1}{10}.
\end{aligned}
\tag{9.40}
$$

We notice that for all the cases (9.35)–(9.39) the symbol J that is used in the algebraic expressions is always $= J_{\mu_i}$. In Cases IV–VI J_{μ_i} is always $< J_{\mu_f}$, but all the cases when $J_{\mu_i} > J_{\mu_f}$ can always be converted to one of the Cases IV–VI by reversing the direction of scattering.

We also notice the negative signs for W_K that appear in Eqs. (9.38)–(9.40). For Rayleigh scattering (Cases I–III) W_K can never be negative, in contrast to the Raman scattering case. A negative value of W_2 means for instance that incoming light that is linearly polarized perpendicular to the scattering plane becomes polarized *parallel* to the scattering plane when emerging from the scattering event. Similarly, a negative value of W_1 means that left-handed circular polarization is converted to right-handed circular polarization.

9.6. Example of Negative Polarizability

To illuminate the physics of negative polarizability, let us consider a concrete case
with a scattering angle of 90°. To explicitly distinguish between the different
magnetic substates m we let them be Zeeman split by a magnetic field that is
perpendicular to the scattering plane. Later we let the field strength go to zero to
retrieve the non-magnetic scattering case (principle of spectroscopic stability).

Let us define the positive Stokes Q direction to be perpendicular to the scatter-
ing plane (and thus parallel to the field vector $\boldsymbol{B}$). Using Eq. (4.48) with $\gamma = \pi/2$
and $\chi = 0$ we obtain the profile functions

$$
\begin{aligned}
H_I &= \tfrac{1}{2}[\,H_0 + \tfrac{1}{2}(H_+ + H_-)\,]\,, \\
H_Q &= \tfrac{1}{2}[\,H_0 - \tfrac{1}{2}(H_+ + H_-)\,]\,, \\
H_U &= H_V = 0
\end{aligned}
\tag{9.41}
$$

for a normal Zeeman triplet. We can directly extend this to the general case of an
anomalous splitting pattern if we replace H_q in Eq. (9.41) with the ϕ_q functions
that were defined by Eq. (6.37). In the case of optically thin radiation the Stokes
parameters of the light beam are proportional to $\phi_{I,Q,U,V}$, so we get

$$
\begin{aligned}
I &\sim \phi_0 + \tfrac{1}{2}(\phi_+ + \phi_-)\,, \\
Q &\sim \phi_0 - \tfrac{1}{2}(\phi_+ + \phi_-)
\end{aligned}
\tag{9.42}
$$

(cf. Sect. 6.5).

As was done in Eq. (6.52) we can further generalize the expressions for ϕ_q to
the case of non-LTE populations of the excited, upper magnetic substates M_u:

$$
\phi_q \sim \sum_{M_\ell, M_u} \rho_{M_u M_u}\, S_q(M_\ell, M_u)\, H_q \,,
\tag{9.43}
$$

where the diagonal density matrix elements $\rho_{M_u M_u}$ represent the relative popula-
tion of the M_u states. S_q is the transition strength between the states represented
by M_u and M_ℓ and is given by Eq. (6.33). $q = M_\ell - M_u$.

In the limit of vanishing field strength $H_+ = H_- = H_0$, which means that
Eqs. (9.42) and (9.43) give us

$$
\begin{aligned}
I &\sim \sum_{M_\ell, M_u} \rho_{M_u M_u}\,[\,S_0 + \tfrac{1}{2}(S_+ + S_-)\,]\,, \\
Q &\sim \sum_{M_\ell, M_u} \rho_{M_u M_u}\,[\,S_0 - \tfrac{1}{2}(S_+ + S_-)\,]\,.
\end{aligned}
\tag{9.44}
$$

The degree of linear polarization of the scattered radiation is $p = Q/I$.

The above expressions describe the emitted radiation without reference to the
absorption, which is the other essential half of the scattering process. The effect
of absorption is however implicitly included in Eq. (9.44), since it is responsible

for the selective population of the M_u states and thus for the values of the density matrix elements of the excited level.

Let us now consider the special case that the incident radiation is linearly polarized perpendicular to the scattering plane (parallel to the magnetic field), i.e., the incident Stokes vector is $\boldsymbol{I}' = I'(1, 1, 0, 0)^\dagger$. Then only absorption transitions with $\Delta M = 0$ are possible. In this case the relative populations $\rho_{M_u M_u}$ of the excited states will only be determined by the populations $\rho_{M_\ell M_\ell}$ of the initial sublevels and the transition strength $S_0(M_\ell, M_u)$. If the initial substates are uncorrelated, as they usually are due to long lifetimes and/or collisions, then the excited M_u substates will also be uncorrelated.

For clarity and illustrative purposes let us now consider the special case when $J_{\mu_i} = 0$, for which there is only one initial substate with $M_\ell = 0$. Then, with our assumption for the polarization of the incident light, only the $M_u = 0$ state will be excited. Eq. (9.44) then simplifies to

$$I \sim S_0(0,0) + \tfrac{1}{2}\left[\, S_+(1,0) + S_-(-1,0)\,\right],$$
$$Q \sim S_0(0,0) - \tfrac{1}{2}\left[\, S_+(1,0) + S_-(-1,0)\,\right], \tag{9.45}$$

provided that $J_{\mu_f} \geq 1$, so that the $M_\ell = \pm 1$ sublevels exist for the final state. When $J_{\mu_f} = 0$ these substates do not exist, with the consequence that $S_\pm = 0$ and therefore $p = Q/I = 1$. This represents the well-known Rayleigh scattering case $J = 0 \to 1 \to 0$, which corresponds to classical dipole-type scattering.

When $J_{\mu_f} \geq 1$ we have two Raman scattering possibilities: $J = 0 \to 1 \to 1$, representing Case V of the preceding section, and $J = 0 \to 1 \to 2$, representing Case VI. In the former case $S_0(0,0) = 0$ and $S_+(1,0) = S_-(-1,0)$, which gives $p = -1$, i.e., the polarization of the scattered radiation is $100\,\%$ linear, *parallel* to the scattering plane. The reason why the polarization plane has been "rotated" by $90°$ in the scattering process is that emission in the π component is forbidden (mathematically a consequence of the properties of the 3-j symbols). This forces all the radiation to be emitted exclusively as σ components, which are polarized perpendicular to the magnetic field vector and thus parallel to the plane of scattering.

In the second Raman scattering case ($J = 0 \to 1 \to 2$), $S_0(0,0) = 0.40$ and $S_\pm(\pm 1, 0) = 0.30$, which according to Eq. (9.45) gives $p = 1/7 \approx 0.14$.

These results are to be compared with those obtained from our algebraic expressions (9.39) and (9.40) for W_2. According to the phase matrix, Eq. (9.19), we get for the scattered radiation when the incident Stokes vector is $\sim (1, 1, 0, 0)^\dagger$

$$I \sim 1 + \tfrac{1}{2} W_2\,,$$
$$Q \sim \tfrac{3}{2} W_2\,, \tag{9.46}$$

and thus

$$p = \frac{3 W_2}{2 + W_2}\,. \tag{9.47}$$

$p = -1$ thus implies that $W_2 = -0.50$, while $p = 1/7$ implies $W_2 = 0.10$, in agreement with Cases V and VI, Eqs. (9.39) (when inserting $J = 0$) and (9.40).

9.7. Upper J-state Interference

In our previous discussion (Sect. 9.4) of the elements W_{ij} of the scattering matrix $\boldsymbol{W}$ and of the expressions that led to the polarizability coefficients W_K, $K = 1, 2$, we disregarded the reduced matrix elements and the profile factors by hiding them in the omitted proportionality factor. This was allowed, since the proportionality factor was the same for all the W_{ij} elements and therefore divided out when forming W_K. The validity of this procedure is however limited to the considered case when only one excited J_m state is involved in the scattering transition. In the case when we need to account for interferences not only between the excited magnetic sublevels m but also between states of different total angular momentum J_m, the reduced matrix elements and profile factors however do not divide out but must be retained throughout the calculations. This means in particular that W_K will vary with wavelength (in contrast to the wavelength-independent expressions of Eqs. (9.35)–(9.40)).

Let us first address the problem of calculating the reduced matrix elements. As shown by Eq. (8.51) the square of the reduced matrix element is proportional to the oscillator strength. This implies that the reduced matrix element alone is proportional to the square root of the oscillator strength times some phase factor. Expressions for this phase factor will be given later in Sect. 9.11, but let us first give some background discussion of the physical situation.

With the Wigner-Eckart theorem of Eq. (7.95) the normal quantum-mechanical matrix element can be factorized into two parts, one reduced matrix element that does not contain any reference to the M quantum number, and a real, M-dependent factor (that contains the 3-j symbol). It is possible to go one step further and do a second reduction of the reduced matrix element, whereby it becomes factorized into two parts, one "doubly reduced" matrix element that only depends on the L and S quantum numbers without reference to J, and one real, J-dependent factor. As the doubly reduced matrix element is common to all the terms in the expressions for W_{ij} (even in the case of J_m-state interference), it can be omitted (or "hidden" in the common proportionality factor). What is then left from the ordinary (singly) reduced matrix element is a real factor, whose magnitude is proportional to the square of the oscillator strength, while its sign depends on the combination of L, S, and J quantum numbers involved. We may thus write

$$\langle J_\mu \,||\, \hat{\boldsymbol{r}} \,||\, J_m \rangle \sim (-1)^{r_{J_\mu J_m}} \sqrt{f_{J_\mu J_m}}\,, \tag{9.48}$$

where $r_{J_\mu J_m}$ is an even or odd integer depending on the values of the L, S, and J quantum numbers. This dependence will be explicitly given in Sect. 9.11.

When we in the following derive explicit expressions for the polarizability in the presence of J-state interference, we will limit ourselves to doing it for the W_2 coefficient. It is straightforward to derive the corresponding expressions for W_1, but this is rarely needed in practice, since the dominating scattering polarization effects are in the linear polarization, governed exclusively by the W_2 coefficient.

For W_2 only the elements W_{11} and W_{14} of the scattering matrix need to be considered, according to Eq. (9.32). To simplify the index notation we will let index ie represent $J_{\mu_i} J_m$, while index fe represents $J_{\mu_f} J_m$ (the letters i, e, and

f thus refer to the initial, excited, and final states, respectively). The previous expressions of Eq. (9.26) can then be generalized (cf. also Eq. (8.117)), to become

$$W_{11} \sim \sum_k \left| \sum_{J_m} (-1)^{r_{ie}+r_{fe}} \sqrt{f_{ie}f_{fe}} \; \Phi_{ef} \right.$$
$$\left. \begin{pmatrix} J_m & J_{\mu_f} & 1 \\ -k & k & 0 \end{pmatrix} \begin{pmatrix} J_m & J_{\mu_i} & 1 \\ -k & k & 0 \end{pmatrix} \right|^2,$$
$$W_{14} \sim \sum_k \left| \sum_{J_m} (-1)^{r_{ie}+r_{fe}} \sqrt{f_{ie}f_{fe}} \; \Phi_{ef} \right.$$
$$\left. \begin{pmatrix} J_m & J_{\mu_f} & 1 \\ -k & k & 0 \end{pmatrix} \begin{pmatrix} J_m & J_{\mu_i} & 1 \\ -k & k-1 & 1 \end{pmatrix} \right|^2. \tag{9.49}$$

The same symmetry arguments that we used for the case without upper J-state interference and which led to Eq. (9.32) for W_K also apply to the present case with J-state interference. Thus Eq. (9.32) is still valid, but W_{11} and W_{14} are given by Eq. (9.49).

In the special case of Rayleigh scattering, when $J_{\mu_f} = J_{\mu_i} = J_\mu$ and $L_f = L_i$,

$$\left[(-1)^{r_{ie}+r_{fe}} \sqrt{f_{ie}f_{fe}} \right]_{\text{Rayleigh}} = f_{J_\mu J_m}. \tag{9.50}$$

The profile factor Φ is given by Eq. (7.90). To formally simplify the expressions we will here omit the damping constant γ, which is often unimportant for problems where the aim is to explore the effects of J_m-state interference. The final expressions that we obtain for W_2 can readily be generalized afterwards by inserting the damping constant again, so the physics is not really restricted by this formal simplification. Omitting γ for the time being means according to Eq. (7.90) that the profile factor can be written as

$$\Phi_{ef} \sim (\nu_{ef} - \nu)^{-1}, \tag{9.51}$$

where ν_{ef} is the resonant frequency of the respective emission transition.

Eq. (9.49) describes the coherent superposition and mixing of states of different J_m number. For the further development of the theory it is convenient to introduce the notation $W_{ij}^{(n)}$ for the W_{ij} that only accounts for a single J_m state $J_m = J_n$ without the phase, oscillator strength, and profile factors. Thus $W_{ij}^{(n)}$ are identical to the W_{ij} that were given by Eq. (9.26) with $J_m = J_n$. They account for the squared, incoherent portions of Eq. (9.49). For the cross (interference) terms that arise from Eq. (9.49) we introduce the notation $W_{ij}^{(u,v)}$, defined by

$$W_{11}^{(u,v)} = \sum_k \begin{pmatrix} J_u & J_{\mu_f} & 1 \\ -k & k & 0 \end{pmatrix} \begin{pmatrix} J_u & J_{\mu_i} & 1 \\ -k & k & 0 \end{pmatrix}$$

$$\begin{pmatrix} J_v & J_{\mu_f} & 1 \\ -k & k & 0 \end{pmatrix} \begin{pmatrix} J_v & J_{\mu_i} & 1 \\ -k & k & 0 \end{pmatrix} ,$$

$$W_{14}^{(u,v)} = \sum_k \begin{pmatrix} J_u & J_{\mu_f} & 1 \\ -k & k & 0 \end{pmatrix} \begin{pmatrix} J_u & J_{\mu_i} & 1 \\ -k & k-1 & 1 \end{pmatrix}$$

$$\begin{pmatrix} J_v & J_{\mu_f} & 1 \\ -k & k & 0 \end{pmatrix} \begin{pmatrix} J_v & J_{\mu_i} & 1 \\ -k & k-1 & 1 \end{pmatrix} . \tag{9.52}$$

When calculating W_2 we form according to Eq. (9.32) $W_{11} - W_{14}$ and $W_{11} + 2W_{14}$. These are expressions of the same form as W_{ij} alone, but with the incoherent $W_{ij}^{(n)}$ coefficients replaced by $W_{11}^{(n)} - W_{14}^{(n)}$ and $W_{11}^{(n)} + 2W_{14}^{(n)}$, and correspondingly for the interference coefficients $W_{ij}^{(u,v)}$. It can be shown through algebraic calculations that

$$W_{11}^{(u,v)} + 2W_{14}^{(u,v)} = 0 , \tag{9.53}$$

which means that the interference terms in the denominator of W_2 and W_1 vanish, while the interference terms in the nominator survive. Eq. (9.53) implies that these interference terms depend on $W_{11}^{(u,v)}$ alone:

$$W_{11}^{(u,v)} - W_{14}^{(u,v)} = 1.5 W_{11}^{(u,v)} . \tag{9.54}$$

Since $\Delta J = 0, \pm 1$ for allowed electric dipole transitions, there can be interference between at most three J_m states. The maximum case of three-state interference can only occur when $J_{\mu_f} = J_{\mu_i}$ and corresponds to interference between Cases I, II, and III of Eqs. (9.35)–(9.37). In the Raman scattering case J_m-state interference may also occur between Cases IV and V (when $|J_{\mu_f} - J_{\mu_i}| = 1$). Case VI is never involved in any J_m-state interference, since only one J_m state is allowed when $|J_{\mu_f} - J_{\mu_i}| = 2$.

9.8. J-state Interference in the Rayleigh Scattering Case

In this section we will formally include the maximum number of three J_m states that may interfere, and use the notation $J_m = J_n$, $n = 1, 2, 3$, to label the interfering states. $n = 1, 2, 3$ correspond to Cases I, II, III of Eqs. (9.35)–(9.37), respectively. If a transition to a given J_m state is forbidden, its contribution to the expressions below will automatically be zero since the corresponding oscillator strength is zero.

For the Rayleigh scattering case ($i = f$) we get from Eqs. (9.49) and (9.50) with the new notations of $W_{ij}^{(n)}$ and $W_{ij}^{(u,v)}$ that were introduced in the preceding section

$$W_{ij} = \sum_{n=1}^{3} f_{fn}^2 \left(\nu_n - \nu\right)^{-2} W_{ij}^{(n)} + 2f_{f1}f_{f2} \left(\nu_1 - \nu\right)^{-1} \left(\nu_2 - \nu\right)^{-1} W_{ij}^{(1,2)}$$

$$+ 2f_{f1}f_{f3} \left(\nu_1 - \nu\right)^{-1} \left(\nu_3 - \nu\right)^{-1} W_{ij}^{(1,3)} + 2f_{f2}f_{f3} \left(\nu_2 - \nu\right)^{-1} \left(\nu_3 - \nu\right)^{-1} W_{ij}^{(2,3)} .$$

$$(9.55)$$

With Eqs. (9.32) and (9.54) we may thus write W_2 as

$$W_2 = \Big[\sum_{n=1}^{3} f_{fn}^2 \, c_{nn} \left(\nu_n - \nu\right)^{-2} + f_{f1}f_{f2} \, c_{12} \left(\nu_1 - \nu\right)^{-1} \left(\nu_2 - \nu\right)^{-1}$$

$$+ f_{f1}f_{f3} \, c_{13} \left(\nu_1 - \nu\right)^{-1} \left(\nu_3 - \nu\right)^{-1} + f_{f2}f_{f3} \, c_{23} \left(\nu_2 - \nu\right)^{-1} \left(\nu_3 - \nu\right)^{-1} \Big]$$

$$\Big/ \sum_{n=1}^{3} f_{fn}^2 \, d_{nn} \left(\nu_n - \nu\right)^{-2} ,$$

$$(9.56)$$

where the coefficients c_{ij} and d_{ii} are formed from combinations of the $W_{ij}^{(n)}$ and $W_{ij}^{(u,v)}$ elements and exclusively depend on the J quantum numbers involved.

$n = 1, 2, 3$ represents an increasing sequence of $J_m = J_n$. Let us as in Eqs. (9.35)–(9.37) use the notation $J_{\mu_f} = J_{\mu_i} = J$. After some fairly extensive algebraic calculations we then get for the coefficients of the squared (incoherent) terms (the diagonal elements of the c_{ij} and d_{ij} matrices)

$$d_{11} = \frac{1}{3(2J-1)} ,$$

$$d_{22} = \frac{1}{3(2J+1)} , \qquad (9.57)$$

$$d_{33} = \frac{1}{3(2J+3)} ,$$

and

$$c_{11} = \frac{(J-1)(2J-3)}{30J(2J-1)(2J+1)} ,$$

$$c_{22} = \frac{(2J-1)(2J+3)}{30J(J+1)(2J+1)} , \qquad (9.58)$$

$$c_{33} = \frac{(J+2)(2J+5)}{30(J+1)(2J+1)(2J+3)} ,$$

while the coefficients for the interference terms are

$$c_{12} = \frac{J-1}{5J(2J+1)} ,$$

$$c_{13} = \frac{2}{5(2J+1)} , \qquad (9.59)$$

$$c_{23} = \frac{J+2}{5(J+1)(2J+1)} .$$

When $\nu = \nu_n$ the influence of the transitions not having the resonant frequency ν_n vanishes, which means that

$$W_2 = c_{nn}/d_{nn} \quad \text{for} \quad \nu = \nu_n \,. \tag{9.60}$$

Inserting the values for c_{nn} and d_{nn} from Eqs. (9.58) and (9.57), we see that the algebraic expressions of Eqs. (9.35)–(9.37) for Cases I, II, III are retrieved when $n = 1, 2, 3$, as expected.

9.9. J-state Interference in the Raman Scattering Case

We need to distinguish between two different situations for Raman scattering: (A) $J_{\mu_f} = J_{\mu_i}$ while $L_f \neq L_i$ (scattering into a different multiplet). Three J_m states may interfere, corresponding to interference between Cases I, II, and III as for Rayleigh scattering. (B) $|J_{\mu_f} - J_{\mu_i}| = 1$. Two J_m states may interfere, corresponding to interference between Cases IV and V. As Case VI corresponds to $|J_{\mu_f} - J_{\mu_i}| = 2$, it cannot be involved in any upper J-state interference.

Let us first turn to case (A) ($J_{\mu_f} = J_{\mu_i}$). In this case the expression for W_2 is the same as Eq. (9.56) for the Rayleigh scattering case, with the exception that the sign factors with parameters r_{ie} and r_{fe} have to be attached to the $W_{ij}^{(u,v)}$ elements and thus also to the interference coefficients c_{uv}, and that the difference between the absorption and emission oscillator strengths has to be accounted for. We then get

$$W_2 = \Big[\sum_{n=1}^{3} f_{in} f_{fn} \, c_{nn} \, (\nu_n - \nu)^{-2} + g_{12} \, c_{12} \, (\nu_1 - \nu)^{-1} \, (\nu_2 - \nu)^{-1}$$
$$+ g_{13} \, c_{13} \, (\nu_1 - \nu)^{-1} \, (\nu_3 - \nu)^{-1} + g_{23} \, c_{23} \, (\nu_2 - \nu)^{-1} \, (\nu_3 - \nu)^{-1} \Big] \tag{9.61}$$
$$\Big/ \sum_{n=1}^{3} f_{in} f_{fn} \, d_{nn} (\nu_n - \nu)^{-2} \,,$$

where

$$g_{uv} = (-1)^{r_{iu} + r_{fu} + r_{iv} + r_{fv}} \, \sqrt{f_{iu} \, f_{fu} \, f_{iv} \, f_{fv}} \,, \tag{9.62}$$

and where d_{nn}, c_{nn}, c_{uv} are given by Eqs. (9.57)–(9.59) as in the Rayleigh scattering case.

Let us next turn to case (B) ($|J_{\mu_f} - J_{\mu_i}| = 1$). If we let $n = 4, 5$ represent Cases IV, V, we get

$$W_2 = \Big[f_{i4} f_{f4} \, c_{44} \, (\nu_4 - \nu)^{-2} + f_{i5} f_{f5} \, c_{55} \, (\nu_5 - \nu)^{-2}$$
$$+ g_{45} \, c_{45} \, (\nu_4 - \nu)^{-1} \, (\nu_5 - \nu)^{-1} \Big] \tag{9.63}$$
$$\Big/ \Big[f_{i4} f_{f4} \, d_{44} \, (\nu_4 - \nu)^{-2} + f_{i5} f_{f5} \, d_{55} \, (\nu_5 - \nu)^{-2} \Big] \,.$$

This expression may represent two different Raman scattering subcases, corresponding to $J_{\mu_f} - J_{\mu_i} = \pm 1$. If we however let

$$J = \min(J_{\mu_i}, J_{\mu_f}),\qquad(9.64)$$

then we can write down the following explicit algebraic expressions that are valid for both these subcases:

$$
\begin{aligned}
d_{44} &= \frac{1}{3(2J+1)}, \\
d_{55} &= \frac{1}{3(2J+3)}, \\
c_{44} &= -\frac{2J-1}{30(J+1)(2J+1)}, \\
c_{55} &= -\frac{2J+5}{30(J+1)(2J+3)}, \\
c_{45} &= -\frac{1}{5(J+1)}\sqrt{\frac{J(J+2)}{(2J+1)(2J+3)}}.
\end{aligned}
\qquad(9.65)
$$

In analogy with Eq. (9.60) for the Rayleigh scattering case we retrieve W_2 of Eqs. (9.38) and (9.39) for Cases IV and V if we in Eq. (9.63) insert $\nu = \nu_4$ or ν_5, which gives $W_2 = c_{44}/d_{44}$ and $W_2 = c_{55}/d_{55}$, respectively.

Finally, for the case when $|J_{\mu_f} - J_{\mu_i}| = 2$, there is as already mentioned no upper J-state interference and therefore no off-diagonal terms of c_{ij} and d_{ij}. Nevertheless we need the single, non-zero diagonal terms of c_{ij} and d_{ij}, i.e., c_{66} and d_{66}, for our later computation of W_2 for complete multiplets (Sect. 9.12 below). d_{66} equals d_{55} of Eq. (9.65), while $c_{66} = 0.1d_{66}$.

9.10. Expressions for the Relative Oscillator Strengths

To derive the polarizability W_2 from Eqs. (9.56), (9.61), and (9.63) we need to calculate the oscillator strengths, which serve as weights for the various terms. However, we do not have to compute the absolute but only the relative oscillator strengths within a multiplet, since the two common scale factors for the oscillator strengths (one scale factor for the multiplet responsible for the absorption process, another scale factor for the multiplet of the emission process) divide out when forming W_2. We may therefore give the relative oscillator strengths as functions of the L, S, and J quantum numbers alone, since the effects of the radial atomic structure are part of the common factor that divides out. For reasons of symmetry we give the relative oscillator strengths in terms of the line strength $S_{ij} = S_{ji}$, from which the relative oscillator strength is obtained through

$$f_{ij} \sim \frac{S_{ij}}{\lambda_{ij}(2J_i + 1)},\qquad(9.66)$$

where λ_{ij} is the wavelength of the transition. As it does not matter to S_{ij} (in contrast to f_{ij}) which is the initial or final level, we may in the expressions below reverse the direction of all the arrows without affecting the form of the expressions.

Thus $L \to L - 1$ can be used for both of the cases $\Delta L = \pm 1$. Because of this symmetry property all the cases that may occur can be covered by giving the expressions for S_{ij} for the two main cases $L \to L - 1$ and $L \to L$, each of which has the three subcases $J \to J + 1$, $J \to J$, and $J \to J - 1$. These expressions for the relative line strength S_{ij}, from Condon and Shortley (1970), are listed below.

$L \to L - 1$, $\quad J \to J + 1$:

$$\frac{(J - L - S)(J - L - S + 1)(J - L + S + 1)(J - L + S + 2)}{J + 1} \,. \tag{9.67}$$

$L \to L - 1$, $\quad J \to J$:

$$\frac{(2J + 1)(L + S - J)(J + L - S)(J + L + S + 1)(J - L + S + 1)}{J(J + 1)} \,. \tag{9.68}$$

$L \to L - 1$, $\quad J \to J - 1$:

$$\frac{(J + L + S)(J + L + S + 1)(J + L - S)(J + L - S - 1)}{J} \,. \tag{9.69}$$

$L \to L$, $\quad J \to J + 1$:

$$\frac{(L + S - J)(J + L + S + 2)(J + L - S + 1)(J - L + S + 1)}{J + 1} \,. \tag{9.70}$$

$L \to L$, $\quad J \to J$:

$$\frac{(2J + 1) \left[J(J + 1) + L(L + 1) - S(S + 1) \right]^2}{J(J + 1)} \,. \tag{9.71}$$

$L \to L$, $\quad J \to J - 1$:

$$\frac{(L + S - J + 1)(J + L - S)(J - L + S)(J + L + S + 1)}{J} \,. \tag{9.72}$$

Only combinations of the L, S, and J quantum numbers for which the triangular condition

$$|L - S| \le J \le |L + S| \tag{9.73}$$

is satisfied are allowed.

9.11. Sign of the Interference Terms

With the Wigner-Eckart theorem, Eq. (7.95), the matrix element $\langle JM \,|\, \hat{r}_q \,|\, J'M' \rangle$ can be factorized into two parts, a reduced matrix element $\langle J \,||\, \hat{r} \,||\, J' \rangle$ that is free from any M dependence, and another part (including a 3-j symbol) that accounts for this M dependence. The total angular momentum that is represented by the quantum number J is formed by vector addition of the orbital angular momentum, represented by L, and the electron spin, represented by S. It is possible to factorize $\langle J \,||\, \hat{r} \,||\, J' \rangle$ such that the spin (S) dependence gets separated from the radial dependence, which is accounted for by the S-independent "doubly reduced" matrix element $\langle L \,||\, \hat{r} \,||\, L' \rangle$. According to Brink and Satchler (1968) we may thus write

$$
\begin{aligned}
\langle J \,||\, \hat{r} \,||\, J' \rangle &= \langle LSJ \,||\, \hat{r} \,||\, L'S'J' \rangle \\
&= (-1)^{L+S+J'+1} \sqrt{2J'+1} \, \sqrt{2L+1} \, \begin{Bmatrix} L & L' & 1 \\ J' & J & S \end{Bmatrix} \langle L \,||\, \hat{r} \,||\, L' \rangle \, .
\end{aligned}
\tag{9.74}
$$

As $\langle L \,||\, \hat{r} \,||\, L' \rangle$ divides out when forming W_2, and as the magnitude of the preceding factor on the right hand side of Eq. (9.74) is implicitly accounted for by expressions (9.67)–(9.72) of the preceding section, our only remaining concern is the sign of this factor. As seen by Eq. (9.74) this sign is determined by the first sign factor (the power of -1) and the sign of the 6-j symbol.

Since the general expressions for the sign are messy, it is more convenient to list the results separately for each case that may occur. This is done below, with index u representing the upper level, index ℓ the lower level. $r_{J_\ell J_u}$ is the sign parameter defined in Eq. (9.48).

CASE A. $L_u = L_\ell - 1$

$$
r_{J_\ell J_u} = J_u - J_\ell + 1 \, .
\tag{9.75}
$$

CASE B.1. $L_u = L_\ell \, , \quad J_u - J_\ell = -1$

$$
r_{J_\ell J_u} = 0 \, .
\tag{9.76}
$$

CASE B.2. $L_u = L_\ell \, , \quad J_u - J_\ell = 0$

$$
\begin{aligned}
r_{J_\ell J_u} = 0 \;\; &\text{if} \;\; J(J+1) \geq S(S+1) - L(L+1) \, , \\
r_{J_\ell J_u} = 1 \;\; &\text{if} \;\; J(J+1) < S(S+1) - L(L+1) \, .
\end{aligned}
\tag{9.77}
$$

CASE B.3. $L_u = L_\ell \, , \quad J_u - J_\ell = 1$

$$
r_{J_\ell J_u} = 1 \, .
\tag{9.78}
$$

CASE C. $L_u = L_\ell + 1$

$$r_{J_\ell J_u} = 0 \, . \tag{9.79}$$

9.12. W_2 for Complete Multiplets

Let us by indices i, e, and f denote the initial, intermediate (excited), and final quantum numbers. W_2, as expressed by Eqs. (9.56), (9.61), and (9.63) above, is then a function of the six quantum numbers $L_{i,e,f}$, S, and $J_{i,f}$ (S does not change within a multiplet, and J_e has already been summed over in our expressions for W_2). We may summarize our previous three expressions for the Rayleigh (Eq. (9.56)) and Raman (Eqs. (9.61) and (9.63)) scattering cases in the single equation

$$W_2(L_{i,e,f} , S \, ; J_i, J_f) = C/D \, , \tag{9.80}$$

where

$$C = \sum_{u=1}^{6} \sum_{v=u}^{6} g_{uv} \, c_{uv} \, (\nu_u - \nu)^{-1} \, (\nu_v - \nu)^{-1} \, ,$$

$$D = \sum_{n=1}^{6} f_{in} f_{fn} \, d_{nn} \, (\nu_n - \nu)^{-2} \, . \tag{9.81}$$

The summations in Eq. (9.81) can only have contributions from the allowed diagonal terms and the allowed off-diagonal terms with (u,v) equal to $(1,2)$, $(1,3)$, $(2,3)$, or $(4,5)$. C and D are implicitly functions of $L_{i,e,f}$, S, and $J_{i,f}$.

To obtain W_2 when accounting for all the contributing transitions within the multiplet of the emission process while keeping the initial J_i number fixed, we have to sum C and D over all possible final states. Since each final J_f state has a multiplicity of $2J_f + 1$ (a factor that is part of the Wigner-Eckart theorem of Eq. (7.95) and which represents the number of magnetic substates),

$$W_2(L_{i,e,f} , S \, ; J_i) = \frac{\sum_{J_f}(2J_f + 1)C(L_{i,e,f} , S \, ; J_i, J_f)}{\sum_{J_f}(2J_f + 1)D(L_{i,e,f} , S \, ; J_i, J_f)} = \frac{C(L_{i,e,f} , S \, ; J_i)}{D(L_{i,e,f} , S \, ; J_i)} \, . \tag{9.82}$$

To account for all the possible contributions in the absorption multiplet we need to sum over all the possible initial J_i numbers as well while attaching the statistical weights $2J_i + 1$ (which are proportional to the diagonal density matrix elements $\rho_{J_i J_i}$, cf. Sect. 8.10):

$$W_2(L_{i,e,f} , S) = \frac{\sum_{J_i}(2J_i + 1) \sum_{J_f}(2J_f + 1)C(L_{i,e,f} , S \, ; J_i, J_f)}{\sum_{J_i}(2J_i + 1) \sum_{J_f}(2J_f + 1)D(L_{i,e,f} , S \, ; J_i, J_f)} = \frac{C(L_{i,e,f} , S)}{D(L_{i,e,f} , S)} \, . \tag{9.83}$$

This summation procedure represents a generalization of Eq. (8.114), where only summation over magnetic substates was discussed. The nominator and denominator have to be summed separately, since they each represent linear combinations of W_{ij} matrix elements.

9.13. Principle of Spectroscopic Stability

The correctness of this jungle of algebraic expressions can be verified by invoking the principle of spectroscopic stability in the limit of vanishing fine-structure splitting. We have previously (Sect. 9.6) made use of this principle by introducing a magnetic field to selectively populate the excited Zeeman sublevels, requiring that non-magnetic scattering should be retrieved in the limit of vanishing magnetic field strength. In the present section the electron spin assumes the previous role of the magnetic field.

The question that we are asking is what value W_2 approaches in the limit of vanishing fine-structure splitting, i.e., when all the resonant frequencies ν_n are made to coincide for all n, or, equivalently, when we consider frequencies ν in the dispersion wings at distances $|\nu_n - \nu|$ from the line centers that are large in comparison with the separation $|\nu_u - \nu_v|$ between the resonant frequencies involved.

In this limiting case all the profile factors $(\nu_n - \nu)^{-2}$ and $(\nu_u - \nu)^{-1}(\nu_v - \nu)^{-1}$ divide out, and we are left with a frequency-independent expression with each term in the nominator and denominator depending in a complex algebraic way on all three quantum numbers L, S, and J, since the oscillator strengths and sign factors have such complicated dependencies. From a mathematical point of view we would therefore expect W_2 to depend on all three numbers L, S, and J.

Physically, however, vanishing fine-structure splitting implies vanishing influence of the electron spin, which, in terms of the corresponding quantum numbers, implies $S \to 0$. In this limit we thus have $S = 0$ and $L = J$. This means that when we form W_2 for the whole multiplet, $W_2(L_{i,e,f}, S)$ of Eq. (9.83), the limiting value should be independent of the value of S used. We may therefore write for arbitrary values of S

$$\lim_{|\nu_u - \nu_v| \to 0} W_2(L_{i,e,f}, S) = W_2(J_{i,e,f}, S = 0), \tag{9.84}$$

where $|\nu_u - \nu_v| \to 0$ for all u and v. When $S = 0$, $J_{i,e,f} = L_{i,e,f}$. The limiting value $W_2(J_{i,e,f}, S = 0)$ is obtained directly from one of the expressions (9.35)–(9.40) (depending on the particular combination of the $J_{i,e,f}$ numbers) if we let $J = \min(L_i, L_f)$ in the respective expression (L assumes the role of J).

As an example, the principle of spectroscopic stability demands that a Raman scattering transition with $(L, S) = (3, 4.5) \to (2, 4.5) \to (1, 4.5)$ must approach $W_1 = -0.50$, $W_2 = 0.10$ in the far dispersion wings, since this follows directly from Case VI, Eq. (9.40), as the transition is of type $J = 1 \to 2 \to 3$ (the values of $W_{1,2}$ are invariant with respect to a reversal of the scattering direction).

As the algebraic expressions that are involved in Eq. (9.83) are very complex, it seems like an "algebraic miracle" that the above principle of spectroscopic stability can really be satisfied, and it would be quite hard to prove it by purely algebraic methods. Instead we have let a computer program that calculates W_2 scan through all possible combinations of L and S quantum numbers, and have thereby verified that the principle of spectroscopic stability is indeed always satisfied. Such a verification in fact constitutes a very powerful test of the correctness of the individual algebraic expressions for the coefficients c_n, c_{uv}, d_n (Eqs. (9.57)–(9.59) and (9.65)), the oscillator strengths $f_{J_\mu J_m}$ (Eqs. (9.67)–(9.72)), and the sign

parameters $r_{J_\mu J_m}$ (Eqs. (9.75)–(9.79)). If any single one of these various parameters were to be computed with the incorrect algorithm, this would immediately be revealed by the test of spectroscopic stability. The interference terms, containing the c_{uv} coefficients, are of course essential. Without any one of them, there would be no spectroscopic stability.

It turns out that the principle of spectroscopic stability has general validity also for scattering transitions from each initial J_i state separately (before we sum over J_i, but after having summed over J_f). We therefore have an even more restrictive condition for spectroscopic stability that always has to be satisfied for both W_1 and W_2:

$$\lim_{|\nu_u - \nu_v| \to 0} W_{1,2}(L_{i,e,f}\,, S\,; J_i) = W_{1,2}(J_{i,e,f},\, S = 0)\,, \qquad (9.85)$$

where $W_{1,2}(L_{i,e,f}\,, S\,; J_i)$ is given by Eq. (9.82).

As a very special case of all this we note that for a transition of the type $S \to P \to S$ ($L = 0 \to 1 \to 0$), W_1 and W_2 always approach the value 1.0 at large distances from the resonant frequencies of the multiplet, i.e., the scattering in the far dispersion wings behaves like classical dipole-type scattering.

9.14. Role of a Background Continuum

The polarization of the background continuous spectrum was treated in Sect. 5.16. In the visible part of the spectrum this polarization, which is mainly due to Thomson scattering at free electrons and Rayleigh scattering at neutral hydrogen, is usually quite small as compared with the polarization of some of the lines. It increases in importance when we go to the blue and UV parts of the spectrum, due to the steep wavelength dependence (λ^{-4}) of Rayleigh scattering at hydrogen (cf. Eq. (5.83)). As shown in Sect. 5.16 both the Rayleigh and Thomson scattering processes are describable as classical dipole-type scattering with frequency-independent $W_{1,2}$ coefficients of unity.

According to Eq. (5.86) the continuous emission vector can be written

$$\boldsymbol{j}_c = \sigma_c \boldsymbol{J}_{\nu,c} + \kappa_c B\nu\, \mathbf{1}\,, \qquad (9.86)$$

where σ_c represents the sum of the Thomson and Rayleigh scattering coefficients as shown by Eq. (5.84). $\boldsymbol{J}_\nu$ is the "average Stokes vector $\boldsymbol{I}_\nu$" as defined by Eq. (5.85). Index c for $\boldsymbol{J}_\nu$ indicates that the phase matrix that is valid for the continuum and is identical to the classical dipole-type phase matrix should be used for the calculation of $\boldsymbol{J}_\nu$.

As seen from Eqs. (6.104), (6.105), (6.94), (5.95), and (5.96), the line emission vector in the line wings can be written as

$$\boldsymbol{j}_L = \sigma_L\, \varphi_\nu\, [\, k_c \boldsymbol{J}_{\nu,L} + (\alpha^{-1} - k_c) J_\nu\, \mathbf{1}\,]\,, \qquad (9.87)$$

where α, given by Eq. (6.90), is the fraction of the line emission events that are part of scattering processes. k_c, given by Eq. (5.67), is the fraction of the scattering processes that occur as coherent scattering. It represents a collisional depolarization factor. σ_L is the line scattering coefficient, which as in Eq. (6.94) is found to be

$$\sigma_L = \alpha \, \frac{h\nu}{4\pi} \, N_u A_{ul} \left/ \int \varphi_\nu J_\nu \, \mathrm{d}\nu \right. , \tag{9.88}$$

where indices u and ℓ refer to the upper and lower levels, respectively. Inserting expression (6.90) for α we obtain

$$\sigma_L = \frac{h\nu}{4\pi} \, N_\ell \, B_{\ell u} \, A_{ul} \left/ \sum_k R_{uk} \right. , \tag{9.89}$$

where we have used the statistical equilibrium relation

$$\sum_k N_k \, R_{ku} = N_u \sum_k R_{uk} \tag{9.90}$$

for the transition rate coefficients. The left hand side of Eq. (9.90) represents the transitions *to* level u, the right hand side the transitions *from* level u.

To arrive at Eqs. (9.87) and (9.88) we have for the parameter e, which occurs in Eqs. (6.105) and (5.95) and is explicitly given by Eq. (5.34), assumed that the incident radiation is unpolarized. We have further replaced $\int \varphi_\nu J_\nu \, \mathrm{d}\nu$ by J_ν, which is a very good approximation in the far line wings. For clarity we have written Eqs. (9.88) and (9.89) for the case of a single line transition only — when several line transitions overlap we simply have to sum over their respective contributions to the line emission vector.

For the average Stokes vector $\boldsymbol{J}_{\nu,L}$ that is based on the phase matrix for the line and is a function of the $W_{1,2}$ polarizability coefficients, we compute $\boldsymbol{J}_\nu$ as defined by Eq. (5.85) with the general phase matrix given by Eq. (9.19). If we omit the $\boldsymbol{E}_{44}$ term in the phase matrix we get the simple relation

$$\boldsymbol{J}_{\nu,L} \approx W_2 \, \boldsymbol{J}_{\nu,c} + (1 - W_2) \, J_\nu \, \boldsymbol{1} \, . \tag{9.91}$$

Omission of the $\boldsymbol{E}_{44}$ term is usually permissible, since scattering of Stokes V is generally unimportant (in comparison with scattering of the linear polarization). Inserting Eq. (9.91) in Eq. (9.87) and using Eq. (9.86), we obtain the total emission vector

$$\begin{aligned}
\boldsymbol{j} = \boldsymbol{j}_L + \boldsymbol{j}_c &= (k_c \, W_2 \, \sigma_L \, \varphi_\nu + \sigma_c) \, \boldsymbol{J}_{\nu,c} \\
&+ [\, \sigma_L \, \varphi_\nu \, (\alpha^{-1} - k_c W_2) \, J_\nu + \kappa_c \, B_\nu \,] \, \boldsymbol{1} \, .
\end{aligned} \tag{9.92}$$

The degree of linear polarization in the Stokes Q direction of the emitted radiation is given by

$$p = j_Q / j_I \, , \tag{9.93}$$

where $j_{I,Q}$ are the first two components of the emission vector $\boldsymbol{j}$. To calculate this degree of polarization we have to evaluate the first two components of the average Stokes vector $\boldsymbol{J}_{\nu,c}$, which we denote $J_{\nu,I}$ and $J_{\nu,Q}$. Using Eqs. (5.68) and (5.60) and assuming that the incident radiation is unpolarized (so that only the first column of the phase matrix needs to be used — the full expressions without this limiting assumption have been given in Stenflo (1976b)), we get

$$\begin{aligned}
J_{\nu,I} &= J_\nu + \tfrac{1}{8}(1 - 3\mu^2)P_\nu \, , \\
J_{\nu,Q} &= \tfrac{3}{8}(1 - \mu^2)P_\nu \, ,
\end{aligned} \tag{9.94}$$

where

$$P_\nu = J_\nu - 3K_\nu \,, \tag{9.95}$$

with

$$K_\nu = \tfrac{1}{2} \int_{-1}^{1} \mu^2 I_\nu \, \mathrm{d}\mu \tag{9.96}$$

being the second order moment of I_ν (while J_ν is the zero order moment). For an isotropic radiation field $P_\nu = 0$. Inserting Eqs. (9.94) in Eq. (9.92) we get

$$\begin{aligned}
j_I =&(\alpha^{-1}\,\sigma_L\,\varphi_\nu + \sigma_c)\,J_\nu + \kappa_c B_\nu \\
&+ \tfrac{1}{8}(1 - 3\mu^2)(k_c\,W_2\,\sigma_L\,\varphi_\nu + \sigma_c)\,P_\nu \,, \\
j_Q =& \ \tfrac{3}{8}(1 - \mu^2)(k_c\,W_2\,\sigma_L\,\varphi_\nu + \sigma_c)\,P_\nu \,.
\end{aligned} \tag{9.97}$$

Usually the last term in j_I may be disregarded, since it is similar in magnitude to j_Q (at the limb, where $\mu = 0$, it is $= \tfrac{1}{3}j_Q$). It is small, since P_ν is generally $\ll J_\nu$. In this case we may write

$$p \approx k_G \left[\alpha\,k_c\,W_2\,r_L + \alpha_c\,(1 - r_L) \right], \tag{9.98}$$

where

$$k_G = \tfrac{3}{8}(1 - \mu^2)\,P_\nu/J_\nu \tag{9.99}$$

represents a "geometrical depolarization factor" (introduced in Stenflo (1982)) that accounts for the polarizability due to the degree of anisotropy of the radiation field,

$$r_L = \frac{\alpha^{-1}\sigma_L\,\varphi_\nu}{\alpha^{-1}\sigma_L\,\varphi_\nu + \sigma_c + \kappa_c B_\nu/J_\nu} \tag{9.100}$$

represents the fraction of the total opacity that is due to line radiation, and

$$\alpha_c = \frac{\sigma_c\,J_\nu}{\sigma_c\,J_\nu + \kappa_c B_\nu} \tag{9.101}$$

represents the fraction of the continuum photons that are due to Rayleigh or Thomson scattering.

So far we have written the explicit expressions only for the case of one line transition (plus background continuum) with a profile function φ_ν. When several transitions (e.g. within a multiplet) contribute, we have to sum over them. Thus, when the polarizability W_2 is calculated, the denominator, which is proportional to the number of line photons, can be expressed as (cf. Eq. (9.32))

$$W_{11} + 2W_{14} \sim \sum_n \alpha_n^{-1}\,\sigma_{L,n}\,\varphi_{\nu,n} \,, \tag{9.102}$$

where the different line contributions in the multiplet are marked by index n. We may now recast Eq. (9.100) in the more general form

$$r_L = \frac{W_{11} + 2W_{14}}{W_{11} + 2W_{14} + a_c} \,, \tag{9.103}$$

where the parameter a_c is independent of wavelength and represents the contribution of the continuum.

It is convenient to introduce

$$W_{2,\,\text{eff}} = W_2\,r_L + b_c(1 - r_L) \tag{9.104}$$

as an "effective" scattering polarizability W_2, which accounts for the effect of the continuum through the wavelength-independent parameters a_c (contained in r_L) and b_c, where

$$b_c = \frac{\alpha_c}{\alpha\,k_c} \tag{9.105}$$

represents the continuum value of $W_{2,\,\text{eff}}$. Then

$$p = \alpha\,k_c\,k_G\,W_{2,\,\text{eff}}\,, \tag{9.106}$$

i.e., the degree of linear polarization p scales in proportion to $W_{2,\,\text{eff}}$. To explore the effect of the continuum on the line polarization one may thus compute $W_{2,\,\text{eff}}$ for different values of the two free parameters a_c and b_c.
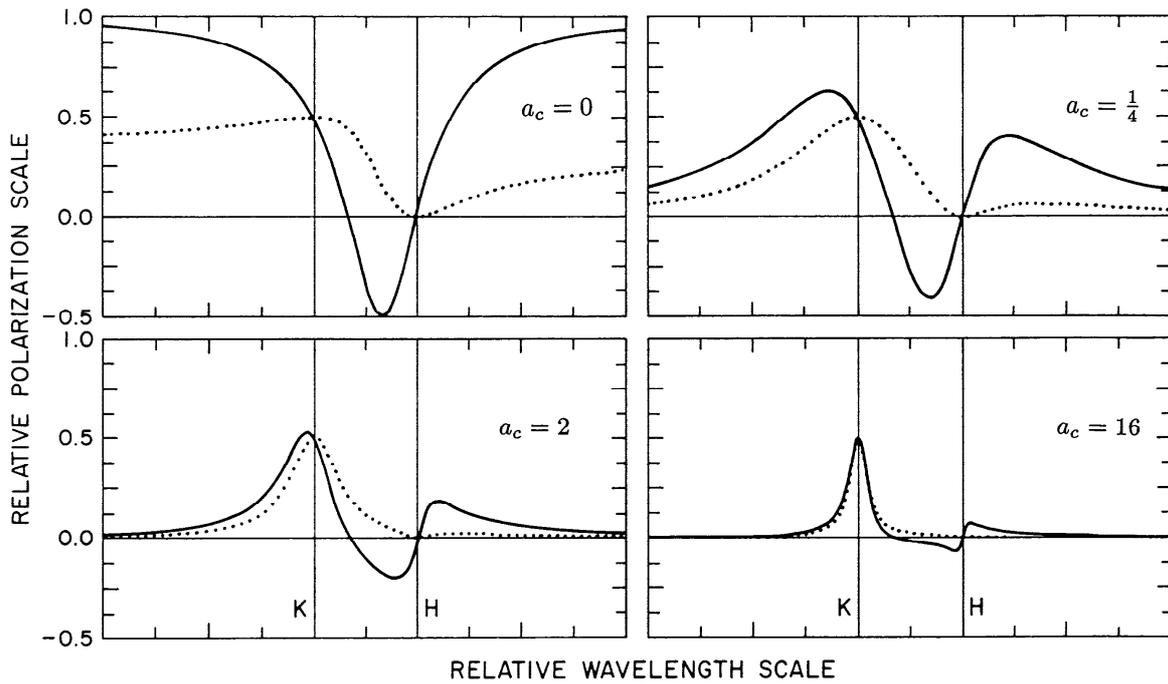

Fig. 9.2. Wavelength variation of $W_{2,\,\text{eff}}$ for a scattering process of the type $S_{\frac{1}{2}} \to P_{\frac{1}{2},\,\frac{3}{2}} \to S_{\frac{1}{2}}$, for different values of the continuum opacity parameter a_c (normalized as described in the text), keeping the continuum polarization parameter $b_c = 0$. The thin vertical lines mark the locations of the two resonant frequencies. The thick solid curve represents $W_{2,\,\text{eff}}$ with J_m-state interference taken into account, while the dotted curve represents the case when this interference has been omitted (incoherent superposition of the two scattering transitions). From Stenflo (1980).

An example of such calculations of $W_{2,\,\mathrm{eff}}$ is given in Figs. 9.2 and 9.3, from Stenflo (1980). The diagrams represent Rayleigh scattering of the type $S_{\frac{1}{2}} \rightarrow P_{\frac{1}{2},\frac{3}{2}} \rightarrow S_{\frac{1}{2}}$ with quantum-mechanical interference between the two $J_m = \frac{1}{2}$ and $\frac{3}{2}$ states. This type of coherent scattering transition is represented by the Ca II K and H lines at 3933 and 3968 Å and by the Na I D_2 and D_1 lines at 5890 and 5896 Å. The normalization used for the continuum parameter a_c is such that for $a_c = 1$ the continuum and line opacities are equal at a frequency that is the average of the two resonant frequencies (i.e., halfways between the two lines).
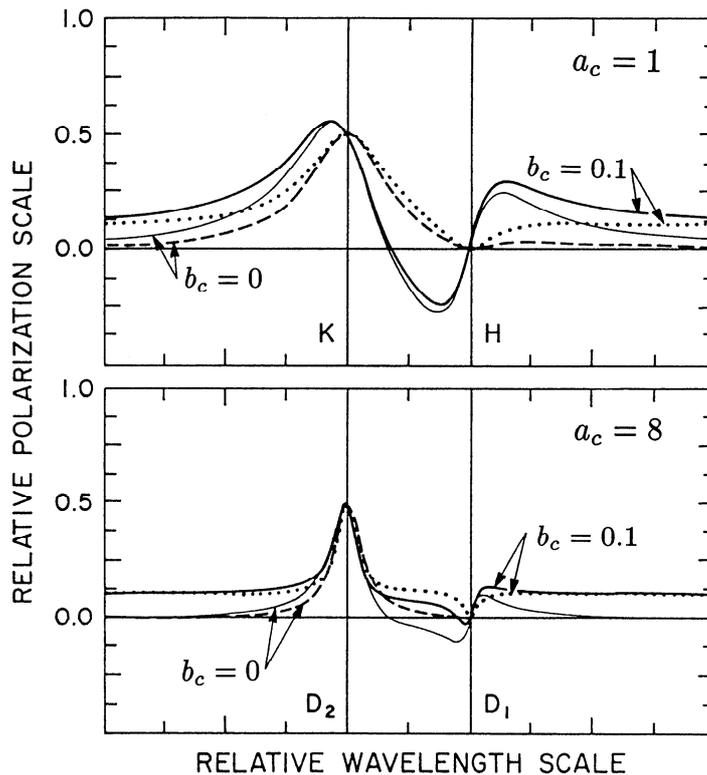

Fig. 9.3. Effect on $W_{2,\,\mathrm{eff}}$ (for the same scattering case as in Fig. 9.2) from varying the continuum polarization parameter b_c. The dotted and dashed curves represent the case when J_m-state interference has been omitted. The choices 1 and 8 for the continuum opacity parameter a_c lead to profile shapes that closely resemble the observed polarization profiles of the Ca II K and H and the Na I D_2 and D_1 lines, respectively. From Stenflo (1980).

In Fig. 9.2 the continuum polarization parameter b_c is set equal to zero, while the opacity parameter a_c is varied. For $a_c = 0$, $W_{2,\,\mathrm{eff}}$ approaches unity in the far line wings, as expected from our discussion of the principle of spectroscopic stability (Sect. 9.13). We see in the figure that this asymptotic limit is not approached when the J_m-state interference term is omitted. When an unpolarized continuum is added, $W_{2,\,\mathrm{eff}}$ asymptotically approaches zero in the distant line wings.

The effect of varying the amount of continuum polarization is illustrated in Fig. 9.3. The asymptotic value of $W_{2,\,\mathrm{eff}}$ in the far wings equals the continuum polarization parameter b_c.
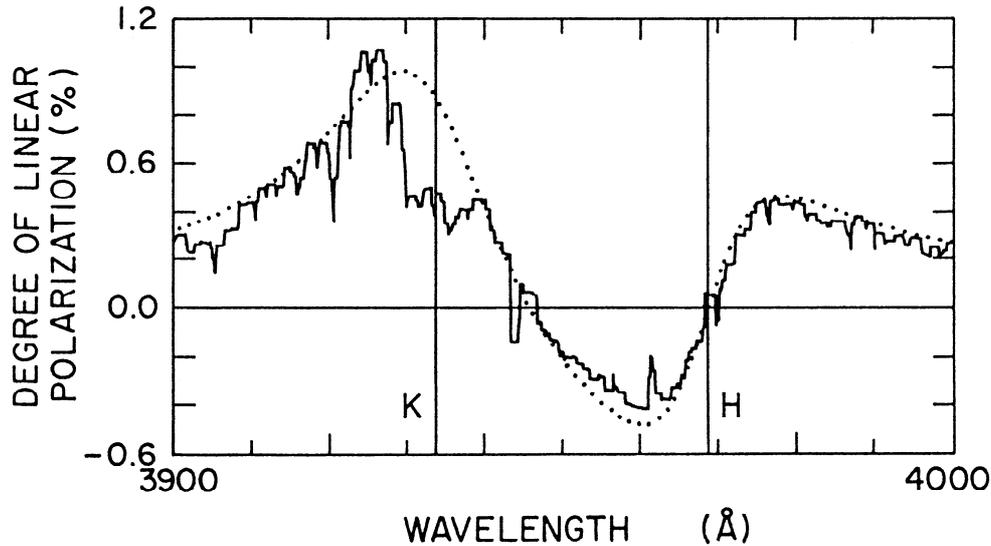
Fig. 9.4. Theoretical fit (dotted curve) to the linear polarization observed at the National Solar Observatory (Kitt Peak) 10 arcsec inside the solar limb at the heliographic north pole (solid curve). The observations have been treated with a 1 Å running window to crudely remove the influence of depolarizing blend lines. Positive values correspond to linear polarization parallel to the solar limb, negative values to polarization perpendicular to the limb. The theoretical curve is based on Eq. (9.106) with the values of the model parameters being $a_c = 1$, $b_c = 0.057$, and $\alpha\, k_c\, k_G = 0.0176$. From Stenflo (1980).

The simple model provided by Eq. (9.106) is able to represent the observations remarkably well. Figure 9.4 shows the model fit (dotted curve) to the observations (solid curve) for the Ca II K and H resonant scattering transition. The parameter values used for the fit are $a_c = 1$ (in terms of the same units as used for Figs. 9.2 and 9.3), $b_c = 0.057$, and $\alpha\, k_c\, k_G = 0.0176$.

9.15. Clarifying Remarks Concerning the Dependence of the Polarizability on Oscillator Strength

According to the semi-classical theory for radiative scattering, Eq. (5.20), the line scattering coefficient σ_L should be proportional to the oscillator strength f_{ij}, not to f_{ij}^2, since the scattering probability is governed by the radiative absorption rate, and the absorbed photons are simply reradiated in the scattering process. We have further seen, through Eq. (9.102), that the denominator of W_2 (cf. Eq. (9.32)), $W_{11} + 2W_{14}$, is proportional to σ_L and thus to f_{ie}, the absorption oscillator strength. This appears to be in contradiction with our expressions (9.56), (9.61), and (9.63) for W_2, where f_{ij} appears *twice* (both as absorption and emission oscillator strength) in each of the various terms in the nominator and denominator. Let us now clarify this situation to show that everything remains consistent, and that the classical expression is indeed reproduced by the quantum-mechanical theory.

In Sects. 8.4 and 8.9 we showed how the correct Einstein transition rates could be obtained from quantum field theory. The same methods can be applied to show how the absolute magnitude of σ_L can be expressed in terms of the Ein-

stein transition rates, starting from the expression (9.4) for the transition rate $1/\tau$ in second-order time-dependent perturbation theory, or, equivalently, from the expressions (8.110) for the scattering amplitudes obtained from quantum-field theory. When inspecting Eqs. (8.111) and (9.15) we see that the scattering amplitude $w_{\alpha\beta}$ contains two matrix elements, one for absorption, the other for emission, each containing a reduced matrix element that is proportional to $\sqrt{f_{ij}}$. When constructing the tensor product $\boldsymbol{w} \otimes \boldsymbol{w}^*$ to get the elements W_{ij} of the $\boldsymbol{W}$ scattering matrix, the oscillator strength will therefore appear *twice* in each element of $\boldsymbol{W}$, although the classical expression (5.20) for σ_L would lead us to believe that the oscillator strength should appear only once.

The source of this apparent confusion lies in the proportionality constant that was omitted in Eqs. (8.111) and (9.15). From Eq. (8.110) we see that this proportionality constant is $\sim a^{-1}$, where a is the normalized damping parameter that is proportional to γ, the inverse lifetime of the excited state. This lifetime is determined by the decay due to spontaneous radiative transitions to any allowed lower level as well as to collisional transitions, as described by Eq. (8.55). In our previous treatment we have implicitly assumed that this damping parameter or inverse lifetime is the same for all terms appearing in W_2, which is justified as all the lower levels are involved in forming the radiative decay rate $\sum_i A_{ji}$. This has allowed us to separate γ^{-1} as a common proportionality constant for the scattering amplitudes $w_{\alpha\beta}$.

In Eq. (9.89) we gave an explicit expression for σ_L in terms of the transition rates, obtained from the non-LTE theory of Chapter 6. The denominator, $\sum_k R_{uk}$, represents the total transition rate away from the upper (excited) level u, and is in fact identical to the inverse lifetime γ. Eq. (9.89) can therefore be rewritten as

$$\sigma_L = \frac{h\nu}{4\pi} \, N_{J_{\mu_i}} \, B_{J_{\mu_i} J_m} \, A_{J_m J_{\mu_f}} \big/ \gamma \,. \tag{9.107}$$

This is indeed the expression we get when deriving the absolute value of σ_L from Eq. (8.110), using the methods of Sects. 8.4 and 8.9.

Since the B and A coefficients are each proportional to an oscillator strength, Eq. (9.107) seems to imply that the oscillator strength appears twice in σ_L. However, the terms that make up γ are also proportional to oscillator strengths. In the special case of a two-level atom with only one radiative decay route, the emission oscillator strength appears both in the nominator and denominator and thus divides out, so that σ_L becomes proportional to $f_{J_{\mu_i} J_m}$ alone, in complete agreement with the semi-classical treatment that led to Eq. (5.20).

9.16. Origin of Partial Polarization in the Scattered Radiation

Any coherent superposition of electromagnetic waves represents radiation that is $100\,\%$ polarized. Mathematically such radiation can be represented by the Jones vector, and as was noted in Sects. 2.6.1 and 4.1, the Jones vector is unable to represent anything that is less than $100\,\%$ polarized. The polarization may be elliptical with arbitrary shape and orientation of the polarization ellipse. In terms

of the Stokes parameters, 100% polarization means that $Q^2 + U^2 + V^2 = I^2$. In quantum terminology we may say that each photon is always 100% polarized.

For a scattering phase matrix $\boldsymbol{P}$ given by Eq. (9.19) with $W_{1,2} = 1$, the scattered radiation is always 100% elliptically polarized whenever the incoming radiation is 100% elliptically polarized. When $W_2 < 1$ the scattered radiation is however only partially polarized. If for instance $W_2 = 0$ the scattered radiation is unpolarized even when the incoming radiation is 100% linearly polarized. On the other hand, when we consider each individual scattering event, both the incoming and scattered photons are always 100% polarized. How can then a scattering matrix with $W_2 < 1$ at all exist?

The source of the partial polarization can be found in the *incoherent* sum in Eq. (8.114) of the scattering matrices (the tensor products of the scattering amplitudes) over all the initial and final magnetic substates μ_i and μ_f. As was shown in Sects. 2.6 and 4.1 the Jones formalism cannot account for partially polarized light, but we need the coherency matrix or Stokes vector formalisms to accomodate an incoherent superposition of stochastically uncorrelated wave trains. While a coherent superposition would still leave the radiation 100% polarized, an incoherent superposition of an ensemble of uncorrelated photon states can result in arbitrary degrees of partial polarization.

If we calculate the scattering phase matrix from the tensor product $\boldsymbol{w} \otimes \boldsymbol{w}$ before any incoherent summation is done, then this phase matrix that represents scattering from an initial magnetic substate μ_i to a final substate μ_f produces scattered radiation that is always 100% elliptically polarized when the incoming radiation is also 100% polarized. The different $\mu_i - \mu_f$ combinations however correspond to different phase matrices. When these matrices are added (which corresponds to an incoherent superposition of uncorrelated scattering events), an average phase matrix that may have $W_{1,2} < 1$ results, which leads to partially polarized scattered radiation.

Scattering from different initial substates (into all the possible μ_f states) produces entirely different amounts of polarization. Let us as an example consider the Rayleigh scattering transition $J = 6 \to 5 \to 6$. According to Eq. (9.35) $W_2 = 0.0577$. If the incident radiation is unpolarized and the scattering angle is $90°$, the polarization of the scattered radiation is according to Eqs. (9.19) and (9.20) $Q/I = P_{21}/P_{11} = \frac{3}{4}W_2/(1 - \frac{1}{4}W_2) = 4.4\%$, with the plane of polarization oriented perpendicular to the scattering plane. If we now consider scattering of unpolarized radiation from only the initial substate $\mu_i = +$ or -6, then $Q/I = -50.6\%$, with the plane of linear polarization oriented *parallel* to the scattering plane. (For the computation of this number we do not have any simple algebraic expressions at our disposal, so we have instead evaluated the 3-j symbols in the scattering amplitudes and then formed P_{21} and P_{11} from products of scattering amplitudes.) Scattering from the initial state with $\mu_i = 0$ on the other hand gives $+30.7\%$ linear polarization oriented perpendicular to the scattering plane. Since the polarization of the scattered radiation is such a sensitive function of μ_i, small deviations from complete redistribution between the initial magnetic substates, i.e., a variation with μ_i of the population $\rho_{\mu_i\mu_i}$, may have considerable effects on the incoherent scattering superposition of the contributions from the various μ_i states.

As a second example we consider scattering for the Rayleigh transition $J = 4 \to 4 \to 4$. While the average Q/I for the complete redistribution case is $+32.0\,\%$ as follows from Eq. (9.36) and the expression for P_{21}/P_{11} above, it is $-63.6\,\%$ for scattering from the $\mu_i = 0$ substate and $+72.9\,\%$ for scattering from $\mu_i = \pm 4$. Such examples may serve as a warning to watch out for the possibility of non-LTE populations of the initial sublevels (while the phase relations between the initial substates or the non-diagonal terms of the density matrix may be neglected).