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2009 J. Phys. A: Math. Theor. 42 445501

(http://iopscience.iop.org/1751-8121/42/44/445501)

IOP PUBLISHING JOURNAL OF PHYSICS A: MATHEMATICAL AND THEORETICAL

J. Phys. A: Math. Theor. **42** (2009) 445501 (19pp) doi:10.1088/1751-8113/42/44/445501

The theory of polarization of radiation emitted by excited atoms

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Received 30 June 2009, in final form 17 September 2009
Published 16 October 2009
Online at stacks.iop.org/JPhysA/42/445501

Abstract
The polarization of radiation emitted in spectral lines provides an important diagnostic tool when the relationship between the mechanisms that excite the atomic or molecular energy levels and the polarization is understood. The gas is assumed to be in statistical equilibrium and we present a general formulation of the theory in which all collisional and radiative excitation and decay processes are included. The colliding particles are assumed to have an anisotropic velocity distribution with cylindrical symmetry and the theory allows for rotation of the axis of observation. Some assumptions made in previous work are removed by the introduction of a completely quantum-mechanical description of the collision processes. Such a theory is important both for the detailed analysis of collision experiments in the laboratory and for the analysis of spectra emitted by astrophysical plasmas.

PACS numbers: 32.30.Jc, 32.70.Fw, 34.10.+x, 95.30.Gv, 95.30.Ky

1. Introduction

In the field of atomic collision physics, analysis of the polarization of photons and electrons produced by a collision is the key to understanding its dynamical evolution.

One of the earliest formulations of the theory of the polarization of spectral line radiation is that by Percival and Seaton [1]. They formulate the problem for electron impact excitation, and consider the cases of pure *LS* coupling, and both fine and hyperfine structure. However, they introduced restrictions that limited the scope for application of their theory, namely that excitation is by a monodirectional unpolarized beam of electrons colliding with unpolarized atoms in the ground state that have zero orbital angular momentum and that the axis of quantization is in the direction of the electron beam. Syms *et al* [2] extended their theory to include degeneracy in the initial energy level, but their agreement with the experiment for hydrogen was limited by the uncertainty of the theoretical scattering data available.

Scattering experiments to measure polarization, orientation and alignment were first carried out in the late 1960s and the experimental and theoretical developments have been described in detail in the book by Andersen and Bartschat [3]. Polarization of Ly_α and Ly_β radiation from hydrogen excited by electron impact has recently been measured by James *et al* [4, 5] for incident electron energies up to 1800 eV and 1000 eV respectively and excellent agreement with close-coupling theory obtained.

A pioneering paper on the use of irreducible tensor techniques and their application to the density matrix for problems of optical pumping and relaxation processes in atoms was published by Omont [6]. Also the use of density matrix theory for many problems in modern atomic physics, including the processes of interest here, has been comprehensively described by Blum [7]. The case of collision-induced alignment in atom–molecule collisions has been considered by Follmeg *et al* [8] who also use a density matrix formulation.

Density matrix theory was first applied to astrophysical plasmas by Sahal–Bréchot in 1977 [9] to simplify the solution of statistical equilibrium equations and hence obtain the polarization of spectral lines emitted from the solar corona. In 1997, Fujimoto and Kazantzev [10] reviewed the theory of plasma polarization spectroscopy and its importance for the analysis of conditions in plasmas such as a tokamak plasma, laser produced plasmas and solar flares. Recently, Landi Degl'Innocenti and Landolfi [11] have published a valuable book which brings together the necessary quantum mechanics, atomic physics, quantum electrodynamics and radiative transfer theory required for a consistent description of all the known physical phenomena that can cause polarization, with particular applications to spectropolarimetry, solar and non-solar.

Polarization of spectral lines has been observed in chromospheric flares and stellar sources and detailed observations have become available with the improvement of measuring devices, see Hénoux *et al* [12, 13] and Vogt and Hénoux [14]. Analyses of solar flares have been carried out for both proton and electron collisions, see Aboudarham *et al* [15], Sahal–Bréchot *et al* [16], Vogt *et al* [17, 18], Balança *et al* [19] and Balança and Feautrier [20]. Their conclusions are that electron bombardment is unlikely to be important and that so far proton beams have not been proved to be an explanation for the observed linear polarization, see Štěpan *et al* [21]. Theoretical studies of x-ray line emission from highly charged ions excited by electron collisions are important for the interpretation of spectra of the solar corona and electron-beam ion trap experiments, see Bensaid *et al* [22] and references therein, where dipole and quadrupole transitions and hyperfine structure may all have to be included.

It is also possible that a neutral beam of protons and electrons of equal velocity may be responsible for the heat transfer between the corona and the chromosphere and may cause the observed polarization of H_α. More detailed observations of the Sun and other sources made with a variety of instruments will soon become available. A general formulation is required that links the anisotropy of the velocity distribution of the colliding particles to the observed polarization. In the present formulation the assumptions that applied in earlier work about the nature of the colliding particles, their angular momenta and their direction relative to that of the observer are removed. This theory used in conjunction with accurate collision data that are now increasingly available will permit the full exploitation of a diagnostic analysis.

The plan of the paper is as follows. In section 2, the general background to the theory is described and in section 3 we introduce irreducible representations of the density matrix and the collisional and radiative rates. In section 4, the analysis of line polarization is presented and in section 5 the relative populations of the target energy levels are described by statistical equilibrium equations. In section 6, detailed expressions required for the evaluation of the collisional excitation and deexcitation rates using a full quantum-mechanical formulation are obtained using a pair-coupling scheme for the target-perturber system. Rates for absorption and spontaneous and induced emission are discussed in section 7. In section 8, we reproduce the result of Follmeg *et al* [8] for the tensorial collision cross section from which the result for LS coupling is extracted. We also modify the theory for the case of monoenergetic beams of colliding particles. In section 9, we give specific results for some special cases of practical interest and finally conclusions follow in section 10.

2. General theoretical background

We consider a beam of particles colliding with an isolated target immersed in an external radiation field. Target energy levels are excited by collisional or radiative processes and subsequently line radiation is emitted which can be observed. In this paper we consider only electric dipole transitions, but the generalization to magnetic dipole transitions is straightforward, see Sahal–Bréchot [9]. We now introduce the following definitions. A photon is emitted in the direction $\hat{\boldsymbol{k}}$ with momentum $\hbar k$, and the particle that excites the atom is incident in the direction $\hat{\boldsymbol{v}}$ with relative velocity v. We define fixed axes $Oxyz$ and vectors $\boldsymbol{k}$ and $\boldsymbol{v}$ have orientations in this fixed frame of reference specified by the spherical polar angles (θ_k, ϕ_k) and (θ_v, ϕ_v), respectively. The quantization axis, Oz, is assumed to be along the axis of cylindrical symmetry of the velocity distribution. We also define two polarization vectors, $\boldsymbol{\epsilon}_\parallel$ and $\boldsymbol{\epsilon}_\perp$, which are such that $\boldsymbol{\epsilon}_\parallel$, $\boldsymbol{\epsilon}_\perp$ and $\hat{\boldsymbol{k}}$ form a right-handed set of mutually orthogonal unit vectors. Circular polarization vectors are then defined by

$$\begin{aligned} \boldsymbol{\epsilon}_1 &= -\frac{1}{\sqrt{2}}(\boldsymbol{\epsilon}_\parallel + \mathrm{i}\boldsymbol{\epsilon}_\perp); \qquad & \boldsymbol{\epsilon}_{-1} &= \frac{1}{\sqrt{2}}(\boldsymbol{\epsilon}_\parallel - \mathrm{i}\boldsymbol{\epsilon}_\perp); \\ \boldsymbol{\epsilon}_\parallel &= \frac{1}{\sqrt{2}}(\boldsymbol{\epsilon}_{-1} - \boldsymbol{\epsilon}_1); & \boldsymbol{\epsilon}_\perp &= \frac{\mathrm{i}}{\sqrt{2}}(\boldsymbol{\epsilon}_1 + \boldsymbol{\epsilon}_{-1}), \end{aligned} \tag{1}$$

see Blum [7]. In the following analysis initial and final states of the target are labelled by i and f respectively. A general linear polarization vector is defined by

$$\boldsymbol{\epsilon} = \cos\beta\,\boldsymbol{\epsilon}_\parallel + \sin\beta\,\boldsymbol{\epsilon}_\perp \tag{2}$$

and the transition probability per unit time for emission of a photon with frequency ν, momentum $\hbar k$ and linear polarization vector $\boldsymbol{\epsilon}$ into solid angle $\mathrm{d}\hat{\boldsymbol{k}}$ is given by

$$A(i \to f; \hat{\boldsymbol{k}}, \boldsymbol{\epsilon})\,\mathrm{d}\hat{\boldsymbol{k}} = \frac{(2\pi\nu)^3}{2\pi c^3\hbar}|\langle i|\boldsymbol{d}\cdot\boldsymbol{\epsilon}|f\rangle|^2\,\mathrm{d}\hat{\boldsymbol{k}}, \tag{3}$$

see, for example, Merzbacher [23] and Messiah [24]. The dipole operator is

$$\boldsymbol{d} = -e\sum_n \boldsymbol{r}_n, \tag{4}$$

where the target electrons have position vectors $\boldsymbol{r}_n$ and energy conservation gives

$$h\nu = E_i - E_f, \tag{5}$$

where E_i and E_f are the energies of the initial and final states of the target respectively. We define the sum over both polarizations by

$$A(i \to f; \hat{\boldsymbol{k}}) \equiv A(i \to f; \hat{\boldsymbol{k}}, \boldsymbol{\epsilon}_\parallel) + A(i \to f; \hat{\boldsymbol{k}}, \boldsymbol{\epsilon}_\perp) = 2A(i \to f; \hat{\boldsymbol{k}}, \boldsymbol{\epsilon}_1) \tag{6}$$

and the total emission rate is obtained by integrating $A(i \to f; \hat{\boldsymbol{k}})$ over all angles of emission so that on using equations (3) and (6) we obtain the Einstein A coefficient

$$A(i \to f) \equiv \int A(i \to f; \hat{\boldsymbol{k}})\,\mathrm{d}\hat{\boldsymbol{k}} = \frac{4(2\pi\nu)^3}{3c^3\hbar}|\langle i|\boldsymbol{d}|f\rangle|^2. \tag{7}$$

The specific intensity $\mathcal{I}(\hat{\boldsymbol{k}}, \nu)$ of the local radiation field is defined as the energy per unit time flowing through unit cross-sectional area perpendicular to the direction $\hat{\boldsymbol{k}}$ per unit solid angle and in unit frequency interval. We then expand $\mathcal{I}(\hat{\boldsymbol{k}}, \nu)$ in terms of multipoles defined by

$$\mathcal{J}_0^\kappa(\nu) = \frac{1}{4\pi}\int \mathcal{I}(\hat{\boldsymbol{k}}, \nu)\, P_\kappa(\cos\theta_k)\, \mathrm{d}\hat{\boldsymbol{k}}, \tag{8}$$

where $P_\kappa(\cos\theta_k)$ is a Legendre polynomial and $\mathcal{J}^0(\nu)$ is the mean intensity. We note that in the notation of Landi Degl'Innocenti and Landolfi [11] equation (5.164),

$$\mathcal{J}_0^0(\nu) = J_0^0(\nu); \qquad \mathcal{J}_0^2(\nu) = \sqrt{2}J_0^2(\nu). \tag{9}$$

The polarization of the emitted radiation can be described by the Stokes parameters (I, Q, U, V), a notation first introduced by Walker [25]. Other notations for these parameters that appear in the literature are (I, M, C, S), see Jones [26] and Perrin [27] and also (s_0, s_1, s_2, s_3) used by Andersen and Bartschat [3]. Blum [7] introduces the parameters $(I, \eta_1, \eta_2, \eta_3)$ where

$$I = s_0; \qquad \eta_1 = s_2/s_0; \qquad \eta_2 = -s_3/s_0; \qquad \eta_3 = s_1/s_0. \tag{10}$$

In this paper, following the work of Sahal–Bréchot [9] we assume that the incident radiation is unpolarized and our choice of reference axes ensures that both Stokes parameters U and V are zero.

We now consider the transition $i \rightarrow f$. If N_i is the number density of atoms in level i, the total intensity $I(\hat{\boldsymbol{k}}, \nu)$ of the transition when a photon of linear polarization $\boldsymbol{\epsilon}$ is emitted is given by

$$I(\hat{\boldsymbol{k}}, \boldsymbol{\epsilon}, \nu) = h\nu\, N_i\, A(i \rightarrow f; \hat{\boldsymbol{k}}, \boldsymbol{\epsilon}), \tag{11}$$

cf [9], where $I(\hat{\boldsymbol{k}}, \nu)$ is in units of energy per unit time per unit volume per unit solid angle per unit frequency interval. The linear polarization of the radiation is described by the fraction

$$P = Q/I; \qquad I = I_\parallel + I_\perp; \qquad Q = I_\parallel - I_\perp \tag{12}$$

and $I_\parallel$ and $I_\perp$ are given by equation (11) with $\boldsymbol{\epsilon} = \boldsymbol{\epsilon}_\parallel$ and $\boldsymbol{\epsilon}_\perp$, respectively. This corresponds to setting $\beta = 0$ and $\pi/2$ in equation (2). Equations (1), (3) and (11) then give

$$I_\parallel \pm I_\perp = \pm\frac{(2\pi\nu)^4}{\pi c^3} N_i\, \Re(\langle i|\boldsymbol{d}\cdot\boldsymbol{\epsilon}_{\pm 1}|f\rangle^* \langle i|\boldsymbol{d}\cdot\boldsymbol{\epsilon}_1|f\rangle). \tag{13}$$

An expression for the number density N_i in equation (11) can be obtained by considering the statistical equilibrium of the populations of the energy levels. If $\mathcal{P}(i \rightarrow f)$ denotes the total probability of a transition $i \rightarrow f$, we have for a system with n levels

$$\sum_{i\neq f} N_i\, \mathcal{P}(i \rightarrow f) = N_f \sum_{i\neq f} \mathcal{P}(f \rightarrow i), \qquad f = 1, 2, \ldots, n, \tag{14}$$

subject to the constraint

$$\sum_{i=1}^{n} N_i = N_T, \tag{15}$$

where N_T is the total number density of the target particles. Equation (14) can be rewritten in the form

$$\sum_{i=1}^{n} N_i\, \mathcal{P}(i \rightarrow f) = 0; \qquad \mathcal{P}(f \rightarrow f) = -\sum_{i\neq f} \mathcal{P}(f \rightarrow i), \tag{16}$$

where $\mathcal{P}(f, f)$ is the relaxation term, see [17]. The matrix $\mathcal{P}$ has elements resulting from collisional and radiative processes, i.e.

$$\mathcal{P}(i \to f) = C(i \to f) + R(i \to f) \tag{17}$$

where rates for excitation/deexcitation have positive/negative signs respectively. Target-perturber collisions can populate or depopulate levels, but the radiative rate corresponds to spontaneous and stimulated emission processes for $E_i > E_f$ and to absorption if $E_i < E_f$. If N_P is the number density of the exciting particles, then the number of transitions $i \to f$ per unit time produced by collisions is given by

$$C(i \to f) = N_P \int \sigma(i \to f; \boldsymbol{v})\, v f(\boldsymbol{v})\, \mathrm{d}\boldsymbol{v}; \qquad \int f(\boldsymbol{v})\, \mathrm{d}\boldsymbol{v} = 1, \tag{18}$$

where the velocity distribution function $f(\boldsymbol{v})$ has cylindrical symmetry and $\sigma(i \to f; \boldsymbol{v})$ is the collision cross section for the transition $i \to f$.

Absorption and stimulated emission are described by B coefficients which are related to the A coefficients in (3) by

$$A(i \to f; \hat{\boldsymbol{k}}, \boldsymbol{\epsilon}) = \frac{2h\nu^3}{c^2} B(i \to f; \hat{\boldsymbol{k}}, \boldsymbol{\epsilon}); \qquad B(f \to i; \hat{\boldsymbol{k}}, \boldsymbol{\epsilon}) = B(i \to f; \hat{\boldsymbol{k}}, \boldsymbol{\epsilon}) \tag{19}$$

and

$$B(i \to f; \hat{\boldsymbol{k}}) \equiv B(i \to f; \hat{\boldsymbol{k}}, \boldsymbol{\epsilon}_\parallel) + B(i \to f; \hat{\boldsymbol{k}}, \boldsymbol{\epsilon}_\perp) = 2B(i \to f; \hat{\boldsymbol{k}}, \boldsymbol{\epsilon}_1). \tag{20}$$

Then on using equations (6), (17) and (20), the number of radiative transitions from level i per unit volume per unit time is given by

$$R(i \to f) = A(i \to f) + \int B(i \to f; \hat{\boldsymbol{k}})\, \mathcal{I}(\hat{\boldsymbol{k}}, \nu)\, \mathrm{d}\hat{\boldsymbol{k}}; \qquad E_i > E_f \tag{21}$$

and

$$R(i \to f) = \int B(i \to f; \hat{\boldsymbol{k}})\, \mathcal{I}(\hat{\boldsymbol{k}}, \nu)\, \mathrm{d}\hat{\boldsymbol{k}}; \qquad E_i < E_f. \tag{22}$$

Finally, it is useful to introduce the density matrix of the system to describe the populations of the energy levels. If ρ is the density operator, see Blum [7], then for a state i

$$N_i = \langle i|\rho|i\rangle\, N_T \tag{23}$$

and we neglect off-diagonal elements of ρ since we will assume that coherences are unimportant. The cylindrical symmetry of $f(\boldsymbol{v})$ means that there are no Zeeman coherences and we assume that non-degenerate energy levels are well separated, see [17].

3. Irreducible tensorial representations

Accurate radiative and collisional data for many systems can now be produced from complex close-coupling calculations involving many coupled channels, cf Burke [28]. In order to be able to use such results in the solution of the statistical equilibrium equations, it is crucial to obtain a general expression for the polarization of the radiation emitted in a transition in which all sums over magnetic quantum numbers have been carried out analytically, so that the only quantities required are independent of orientation. This can be achieved by introducing irreducible tensorial representations of the various physical quantities in equations (16) and (17).

We specify a state of the target by the quantum numbers αJM where J and M refer to the total momentum and α denotes all other relevant quantum numbers. The population of the state αJM is given by (23), i.e.

$$N_{\alpha JM} = N_{\alpha J\,-M} = \langle \alpha JM|\rho|\alpha JM\rangle\, N_T \tag{24}$$

since Stokes parameters U and V are both zero and only state alignment can occur. We now introduce multipolar expansion elements $\rho_0^\lambda(\alpha J)$ defined in [7] by

$$\rho_0^\lambda(\alpha J) = \sum_M (-1)^{J-M}(2\lambda+1)^{\frac{1}{2}} \begin{pmatrix} J & \lambda & J \\ -M & 0 & M \end{pmatrix} \langle \alpha JM|\rho|\alpha JM\rangle, \tag{25}$$

which are identical to the elements ${}^{\alpha J\alpha J}\rho_0^\lambda$ defined by Sahal–Bréchot [9]. The properties of the $3j$ coefficient $\left(\begin{smallmatrix} a & b & c \\ d & e & f \end{smallmatrix}\right)$ are listed in equations (A.1) and (A.2) and equation (25) may be inverted to give

$$\langle \alpha JM|\rho|\alpha JM\rangle = \sum_\lambda (-1)^{J-M}(2\lambda+1)^{\frac{1}{2}} \begin{pmatrix} J & \lambda & J \\ -M & 0 & M \end{pmatrix} \rho_0^\lambda(\alpha J), \tag{26}$$

where (24) implies that λ must be even. On using the Wigner–Eckhart theorem (A.3), $\rho_0^\lambda(\alpha J)$ can also be expressed in terms of a reduced matrix element, i.e.

$$(2\lambda+1)^{\frac{1}{2}}\,\rho_0^\lambda(\alpha J) = \langle \alpha J\|\rho(\lambda)\|\alpha J\rangle. \tag{27}$$

Quantities of the type $U(i \to f)$ where U denotes $\mathcal{P}$, C, R, σ, A or B, see (7), (17), (18) and (6), can also be expanded in terms of multipoles, so that

$$U(\alpha JM \to \alpha' J'M') = \sum_{\lambda\lambda'} (-1)^{J-M+J'-M'}\,[(2\lambda+1)(2\lambda'+1)]^{\frac{1}{2}} \times \begin{pmatrix} J & \lambda & J \\ -M & 0 & M \end{pmatrix} \begin{pmatrix} J' & \lambda' & J' \\ -M' & 0 & M' \end{pmatrix} U^{\lambda\lambda'}(\alpha J \to \alpha' J') \tag{28}$$

and on inverting (28)

$$U^{\lambda\lambda'}(\alpha J \to \alpha' J') = \sum_{MM'} (-1)^{J-M+J'-M'}\,[(2\lambda+1)(2\lambda'+1)]^{\frac{1}{2}} \times \begin{pmatrix} J & \lambda & J \\ -M & 0 & M \end{pmatrix} \begin{pmatrix} J' & \lambda' & J' \\ -M' & 0 & M' \end{pmatrix} U(\alpha JM \to \alpha' J'M'). \tag{29}$$

Also since $f(\boldsymbol{v})$ has cylindrical symmetry about the quantization axis, we can expand the velocity distribution so that

$$f(\boldsymbol{v}) = \frac{1}{4\pi}\sum_\kappa (2\kappa+1) f_0^\kappa(v) P_\kappa(\cos\theta_v); \qquad \int_0^\infty v^2 f_0^0(v)\,\mathrm{d}v = 1, \tag{30}$$

where only even values are included in the sum over κ. We then introduce the tensorial collision cross section ${}^\kappa\sigma^{\lambda\lambda'}(\alpha J \to \alpha' J'; v)$ defined by

$${}^\kappa\sigma^{\lambda\lambda'}(\alpha J \to \alpha' J'; v) = \frac{1}{4\pi}\int \sigma^{\lambda\lambda'}(\alpha J \to \alpha' J'; \boldsymbol{v})\, P_\kappa(\cos\theta_v)\,\mathrm{d}\hat{\boldsymbol{v}} \tag{31}$$

and so

$$\sigma^{\lambda\lambda'}(\alpha J \to \alpha' J'; \boldsymbol{v}) = \sum_\kappa (2\kappa+1)\,{}^\kappa\sigma^{\lambda\lambda'}(\alpha J \to \alpha' J'; v)\, P_\kappa(\cos\theta_v). \tag{32}$$

We can define similar quantities for the radiative transitions and from equations (8), (20) and (29) we have that

$$\mathcal{I}(\hat{\boldsymbol{k}}, \nu) = \sum_\kappa (2\kappa+1)\mathcal{J}_0^\kappa(\nu) P_\kappa(\cos\theta_k), \tag{33}$$

$${}^\kappa B^{\lambda\lambda'}(\alpha J \to \alpha' J') = \int B^{\lambda\lambda'}(\alpha J \to \alpha' J'; \hat{\boldsymbol{k}}) P_\kappa(\cos\theta_k)\,\mathrm{d}\hat{\boldsymbol{k}} \tag{34}$$

and so

$$B^{\lambda\lambda'}(\alpha J \to \alpha' J'; \hat{\boldsymbol{k}}) = \frac{1}{4\pi}\sum_\kappa (2\kappa+1)\,{}^\kappa B^{\lambda\lambda'}(\alpha J \to \alpha' J')\, P_\kappa(\cos\theta_k). \tag{35}$$

4. Analysis of line polarization

The intensity of the line radiation is described by (13) and we assume that the initial and final states have degenerate substates specified by the quantum numbers $\alpha_i J_i M_i$ and $\alpha_f J_f M_f$, respectively. We introduce the rotation operator $\mathcal{D}(\hat{\boldsymbol{k}})$ so that

$$\boldsymbol{d}\cdot\boldsymbol{\epsilon}_\mu = \left(\frac{4\pi}{3}\right)^{\frac{1}{2}} \sum_{\mu'} \mathcal{D}^{(1)}_{\mu'\mu}(\hat{\boldsymbol{k}})\, d\, Y_{1\mu'}(\hat{\boldsymbol{d}}), \qquad \mu = \pm 1, \tag{36}$$

and therefore on using (A.3), we obtain

$$\langle \alpha_i J_i M_i | \boldsymbol{d}\cdot\boldsymbol{\epsilon}_\mu | \alpha_f J_f M_f\rangle = \sum_{\mu'} \mathcal{D}^{(1)}_{\mu'\mu}(\hat{\boldsymbol{k}}) (-1)^{J_i - M_i} \begin{pmatrix} J_i & 1 & J_f \\ -M_i & \mu' & M_f \end{pmatrix} \langle \alpha_i J_i \| \boldsymbol{d} \| \alpha_f J_f\rangle. \tag{37}$$

Results (37) and (A.4) can then be combined so that

$$\langle \alpha_i J_i M_i | \boldsymbol{d}\cdot\boldsymbol{\epsilon}_\mu | \alpha_f J_f M_f\rangle^* \langle \alpha_i J_i M_i | \boldsymbol{d}\cdot\boldsymbol{\epsilon}_1 | \alpha_f J_f M_f\rangle = |\langle \alpha_i J_i \| \boldsymbol{d} \| \alpha_f J_f\rangle|^2\, \mathcal{T}(J_i, J_f, \mu; \hat{\boldsymbol{k}}), \tag{38}$$

where

$$\mathcal{T}(J_i, J_f, \mu; \hat{\boldsymbol{k}}) \equiv \sum_{\mu'} (-1)^{\mu'-\mu} \left[\begin{pmatrix} J_i & 1 & J_f \\ -M_i & \mu' & M_f \end{pmatrix}\right]^2 \times \sum_{lm} (2l+1) \begin{pmatrix} 1 & 1 & l \\ -\mu' & \mu' & 0 \end{pmatrix} \mathcal{D}^{(l)*}_{0m}(\hat{\boldsymbol{k}}) \begin{pmatrix} 1 & 1 & l \\ -\mu & 1 & m \end{pmatrix}. \tag{39}$$

We now set $\mu = 1$ in (39), use (3), (6), (38), (A.2) and (A.5), integrate over all angles of emission and sum over μ' and M_f. Then the Einstein A coefficient for the transition $\alpha_i J_i \to \alpha_f J_f$ is given by

$$A(\alpha_i J_i \to \alpha_f J_f) = \frac{4(2\pi\nu)^3}{3c^3\hbar} \frac{1}{(2J_i+1)} |\langle \alpha_i J_i \| \boldsymbol{d} \| \alpha_f J_f\rangle|^2. \tag{40}$$

In order to evaluate $I_\parallel \pm I_\perp$ in (13) we require the sum

$$N_T \sum_{M_i M_f \lambda} \rho_0^\lambda(\alpha_i J_i)\, (-1)^{J_i - M_i}\, (2\lambda+1)^{\frac{1}{2}} \begin{pmatrix} J_i & \lambda & J_i \\ -M_i & 0 & M_i \end{pmatrix} \times \langle \alpha_i J_i M_i | \boldsymbol{d}\cdot\boldsymbol{\epsilon}_\mu | \alpha_f J_f M_f\rangle^* \langle \alpha_i J_i M_i | \boldsymbol{d}\cdot\boldsymbol{\epsilon}_1 | \alpha_f J_f M_f\rangle \tag{41}$$

where we have used (24) and (26). On combining (38), (39) and (41), the sums over μ' and M_f can be evaluated using (A.6) and then the sum over M_i follows from (A.2). Finally using (40), (13) becomes

$$I_\parallel + \mu I_\perp = \mu \frac{h\nu}{4\pi} N_T\, 3(2J_i+1)\, (-1)^{J_i+J_f+1} A(\alpha_i J_i \to \alpha_f J_f) \sum_\lambda \rho_0^\lambda(\alpha_i J_i)\, (2\lambda+1)^{\frac{1}{2}} \times \begin{Bmatrix} J_i & J_i & \lambda \\ 1 & 1 & J_f \end{Bmatrix} \begin{pmatrix} 1 & 1 & \lambda \\ -\mu & 1 & \mu-1 \end{pmatrix} \mathcal{D}^{(\lambda)*}_{0\mu-1}(\hat{\boldsymbol{k}}); \qquad \mu = \pm 1. \tag{42}$$

We can take $\phi_k = 0$ without loss of generality and so the sum in (42) is real, see (A.5). Therefore, by considering the cases $\mu = 1, \lambda = 0, 2$ and $\mu = -1, \lambda = 2$ in (42) and using (A.5), the polarization fraction in (12) is given by

$$P = \frac{-3\sin^2\theta_k\, \eta}{1 + (3\cos^2\theta_k - 1)\eta}, \tag{43}$$

where for a radiative transition $\alpha_i J_i \to \alpha_f J_f$

$$\eta \equiv \frac{1}{2\sqrt{2}} \frac{\begin{Bmatrix} J_i & J_i & 2 \\ 1 & 1 & J_f \end{Bmatrix}}{\begin{Bmatrix} J_i & J_i & 0 \\ 1 & 1 & J_f \end{Bmatrix}} \frac{\rho_0^2(\alpha_i J_i)}{\rho_0^0(\alpha_i J_i)}, \tag{44}$$

cf Sahal–Bréchot [9], equations (4) and (14) and Andersen and Bartschat [3] equation (7.6). If there are several levels $\alpha_i J_i$ and $\alpha_f J_f$ that are essentially degenerate, then (44) must be replaced by

$$\eta \equiv \frac{1}{2\sqrt{2}} \frac{\sum_{\alpha_i J_i \alpha_f J_f} \Omega_2(J_i \to J_f)\, A(\alpha_i J_i \to \alpha_f J_f)\, \rho_0^2(\alpha_i J_i)}{\sum_{\alpha_i J_i \alpha_f J_f} \Omega_0(J_i \to J_f)\, A(\alpha_i J_i \to \alpha_f J_f)\, \rho_0^0(\alpha_i J_i)}, \tag{45}$$

where

$$\Omega_\lambda(J_i \to J_f) \equiv (-1)^{J_i + J_f + 1} (2J_i + 1) \begin{Bmatrix} J_i & J_i & \lambda \\ 1 & 1 & J_f \end{Bmatrix} \tag{46}$$

in agreement with the result given by Vogt *et al* [17].

5. Statistical equilibrium equations

5.1. General formulation

From equations (18), (24), (26) and (28), we obtain

$$\begin{aligned}\sum_i N_i C(i \to f) &= N_T N_P \sum_{\alpha_i J_i M_i} \langle \alpha_i J_i M_i | \rho | \alpha_i J_i M_i \rangle \int \sigma(\alpha_i J_i M_i \to \alpha_f J_f M_f; \boldsymbol{v})\, v f(\boldsymbol{v})\, \mathrm{d}\boldsymbol{v} \\ &= N_T N_P \sum_{\alpha_i J_i \lambda\lambda'\lambda''} [(2\lambda+1)(2\lambda'+1)(2\lambda''+1)]^{\frac{1}{2}}\, \rho_0^\lambda(\alpha_i J_i) \\ &\quad \times \sum_{M_i} (-1)^{J_f - M_f} \begin{pmatrix} J_i & \lambda & J_i \\ -M_i & 0 & M_i \end{pmatrix} \begin{pmatrix} J_i & \lambda' & J_i \\ -M_i & 0 & M_i \end{pmatrix} \begin{pmatrix} J_f & \lambda'' & J_f \\ -M_f & 0 & M_f \end{pmatrix} \\ &\quad \times \int \sigma^{\lambda'\lambda''}(\alpha_i J_i \to \alpha_f J_f; \boldsymbol{v})\, v f(\boldsymbol{v})\, \mathrm{d}\boldsymbol{v}.\end{aligned} \tag{47}$$

We use (A.2) to evaluate the sum over M_i in (47) and so

$$\begin{aligned}\sum_i N_i C(i \to f) &= N_T N_P \sum_{\alpha_i J_i \lambda\lambda'} (-1)^{J_f - M_f} (2\lambda'+1)^{\frac{1}{2}} \begin{pmatrix} J_f & \lambda' & J_f \\ -M_f & 0 & M_f \end{pmatrix} \rho_0^\lambda(\alpha_i J_i) \\ &\quad \times \int \sigma^{\lambda\lambda'}(\alpha_i J_i \to \alpha_f J_f; \boldsymbol{v})\, v f(\boldsymbol{v})\, \mathrm{d}\boldsymbol{v},\end{aligned} \tag{48}$$

where from equations (30) and (32) we obtain

$$\begin{aligned}\int \sigma^{\lambda\lambda'}(\alpha_i J_i \to \alpha_f J_f; \boldsymbol{v})\, v f(\boldsymbol{v})\, \mathrm{d}\boldsymbol{v} &= \sum_\kappa (2\kappa + 1) \\ &\quad \times \int {}^\kappa\sigma^{\lambda\lambda'}(\alpha_i J_i \to \alpha_f J_f; v)\, f_0^\kappa(v)\, v^3\, \mathrm{d}v.\end{aligned} \tag{49}$$

Similarly, from equations (6), (21), (22), (26), (33) and (34)

$$\begin{aligned}\sum_i N_i R(i \to f) &= N_T \sum_{\alpha_i J_i \lambda\lambda'} (-1)^{J_f - M_f} (2\lambda'+1)^{\frac{1}{2}} \begin{pmatrix} J_f & \lambda' & J_f \\ -M_f & 0 & M_f \end{pmatrix} \rho_0^\lambda(\alpha_i J_i) \\ &\quad \times \int B^{\lambda\lambda'}(\alpha_i J_i \to \alpha_f J_f; \hat{\boldsymbol{k}})\, \mathcal{I}(\hat{\boldsymbol{k}}, \nu)\, \mathrm{d}\hat{\boldsymbol{k}},\end{aligned} \tag{50}$$

cf (48), where because we have set $\phi_k = 0$

$$\int B^{\lambda\lambda'}(\alpha_i J_i \to \alpha_f J_f; \hat{\boldsymbol{k}})\, \mathcal{I}(\hat{\boldsymbol{k}}, \nu)\, \mathrm{d}\hat{\boldsymbol{k}} = \sum_{\kappa} (2\kappa + 1)\, {}^{\kappa}B^{\lambda\lambda'}(\alpha_i J_i \to \alpha_f J_f)\, \mathcal{J}_0^{\kappa}(\nu). \tag{51}$$

Finally on setting $U = \mathcal{P}$ in (29) and also using relations (16), (17), (26), (48) and (50), the statistical equilibrium equations (16) can be rewritten in the form

$$\sum_{\alpha_i J_i \lambda} \mathcal{P}^{\lambda\lambda'}(\alpha_i J_i \to \alpha_f J_f)\, \rho_0^{\lambda}(\alpha_i J_i) = 0. \tag{52}$$

This completes the analysis required for the polarization of the radiation as specified by equations (12)–(14).

5.2. Approximate solutions

If collisional excitation and spontaneous emission are the dominant processes so that the other processes can be neglected, the statistical equilibrium equations simplify considerably. We assume that the excitation of states $\alpha_i J_i M_i$ is only by collisions from initial states $\alpha_g J_g M_g$, followed by decay through spontaneous emission to states $\alpha_f J_f M_f$. Then using (14) and (29), (52) reduces to

$$\sum_{\alpha_g J_g \lambda} \rho_0^{\lambda}(\alpha_g J_g)\, C_{\mathrm{trn}}^{\lambda\lambda'}(\alpha_g J_g \to \alpha_i J_i) = \rho_0^{\lambda'}(\alpha_i J_i) \sum_{\alpha_f J_f} A(\alpha_i J_i \to \alpha_f J_f), \tag{53}$$

where the subscript 'trn' is introduced to emphasize that transitions between distinct states of the target are being considered. This gives an explicit expression for $\rho_0^{\lambda'}(\alpha_i J_i)$ which can then be used in (44) and (45) to give the polarization of the radiation. If in addition, the initial states are equally populated, then from (25) and (26) $N_{\alpha_g J_g M_g} \equiv N_{\alpha_g J_g}/(2J_g + 1)$, say, so that

$$\rho_0^{\lambda}(\alpha_g J_g) = \delta_{\lambda 0}\, (2J_g + 1)^{\frac{1}{2}}\, N_{\alpha_g J_g} \big/ N_T. \tag{54}$$

6. Tensorial cross sections

6.1. Collisional transitions

We shall assume that the hyperfine structure of the target is not important but in many applications its fine structure cannot be neglected. In this section, if we specify the state i of the target by the quantum numbers $\alpha_i J_i M_i$ and the corresponding colliding particle by quantum numbers $l_i m_i s m_s$, then the cross section for the collisional excitation $i \to f$ in an uncoupled representation is

$$\begin{aligned}\sigma_{\mathrm{trn}}(\alpha_i J_i M_i \to \alpha_f J_f M_f; \boldsymbol{v}) = {} & \left(\frac{2\pi\hbar}{\mathcal{M}v}\right)^2 \frac{1}{(2s+1)} \sum_{l_i m_i l_i' m_i'} \sum_{l_f m_f m_s m_s'} \\ & \times \mathrm{i}^{l_i - l_i'}\, Y^*_{l_i m_i}(\theta_v, \phi_v) Y_{l_i' m_i'}(\theta_v, \phi_v) \\ & \times \langle \alpha_i J_i M_i l_i m_i s m_s | T | \alpha_f J_f M_f l_f m_f s m_s' \rangle \\ & \times \langle \alpha_i J_i M_i l_i' m_i' s m_s | T | \alpha_f J_f M_f l_f m_f s m_s' \rangle^*,\end{aligned} \tag{55}$$

cf Geltman [29]. In equation (55), $\mathcal{M}$ is the reduced mass of the target–particle system and T is the transition matrix evaluated for the total energy of the system given by

$$\mathcal{E} = E_i + \tfrac{1}{2}\mathcal{M}v^2. \tag{56}$$

We use a pair-coupling notation in which the target quantum numbers $J_i M_i$ and $J_f M_f$ couple with $l_i m_i$, $l_i' m_i'$ and $l_f m_f$ respectively to give quantum numbers $k_i \mu_i$, $k_i' \mu_i'$ and $k_f \mu_f$. These then couple with the spin quantum numbers $s m_s$ and $s m_s'$ of the scattered particle to give the total angular momentum quantum numbers JM and $J'M'$. The transformation of the transition matrix is given by

$$\langle \alpha_i J_i M_i l_i m_i s m_s | T | \alpha_f J_f M_f l_f m_f s m_s' \rangle = \sum_{JM} \sum_{k_i \mu_i k_f \mu_f} C^{J_i l_i k_i}_{M_i m_i \mu_i} C^{k_i s J}_{\mu_i m_s M} C^{J_f l_f k_f}_{M_f m_f \mu_f} C^{k_f s J}_{\mu_f m_s' M} \times \langle \alpha_i J_i l_i k_i s J | T | \alpha_f J_f l_f k_f s J \rangle \qquad (57)$$

where C^{abc}_{def} denotes a Clebsch–Gordon coefficient, see (A.1). On substituting equation (57) into equation (55) we obtain

$$\sigma_{\rm trn}(\alpha_i J_i M_i \to \alpha_f J_f M_f; \boldsymbol{v}) = \left(\frac{2\pi\hbar}{\mathcal{M}v}\right)^2 \sum_{JJ'} \sum_{l_i m_i l_i' m_i' l_f} \sum_{k_i k_i' k_f k_f'} \mathcal{S}(M_i, M_f, m_i, m_i') \times {\rm i}^{l_i - l_i'} Y^*_{l_i m_i}(\theta_v, \phi_v) Y_{l_i' m_i'}(\theta_v, \phi_v) \times \langle \alpha_i J_i l_i k_i s J | T | \alpha_f J_f l_f k_f s J \rangle \langle \alpha_i J_i l_i' k_i' s J' | T | \alpha_f J_f l_f k_f' s J' \rangle^*, \qquad (58)$$

where

$$\mathcal{S}(M_i, M_f, m_i, m_i') \equiv \frac{1}{(2s+1)} \sum_{MM'} \sum_{m_f m_s m_s'} \sum_{\mu_i \mu_i' \mu_f \mu_f'} C^{J_i l_i k_i}_{M_i m_i \mu_i} C^{J_i l_i' k_i'}_{M_i m_i' \mu_i'} \times C^{J_f l_f k_f}_{M_f m_f \mu_f} C^{J_f l_f k_f'}_{M_f m_f \mu_f'} C^{k_i s J}_{\mu_i m_s M} C^{k_i' s J'}_{\mu_i' m_s M'} C^{k_f s J}_{\mu_f m_s' M} C^{k_f' s J'}_{\mu_f' m_s' M'}. \qquad (59)$$

On using (29), we obtain

$$\sigma^{\lambda\lambda'}_{\rm trn}(\alpha_i J_i \to \alpha_f J_f; \boldsymbol{v}) = \sum_{M_i M_f} (-1)^{J_i - M_i + J_f - M_f} [(2\lambda+1)(2\lambda'+1)]^{\frac{1}{2}} \times \begin{pmatrix} J_i & \lambda & J_i \\ -M_i & 0 & M_i \end{pmatrix} \begin{pmatrix} J_f & \lambda' & J_f \\ -M_f & 0 & M_f \end{pmatrix} \sigma_{\rm trn}(\alpha_i J_i M_i \to \alpha_f J_f M_f; \boldsymbol{v}) \qquad (60)$$

and using (A.6) the sums over $M_f m_f$, $\mu_f m_s'$ and $MM'm_s$ in (58)–(60) can be carried out sequentially to yield

$$\sigma^{\lambda\lambda'}_{\rm trn}(\alpha_i J_i \to \alpha_f J_f; \boldsymbol{v}) = \left(\frac{2\pi\hbar}{\mathcal{M}v}\right)^2 \frac{1}{(2s+1)} \sum_{JJ'} \sum_{l_i l_i' l_f} \sum_{k_i k_i' k_f k_f'} \sum_{M_i m_i m_i' \mu_i \mu_i'} \times C^{J_i l_i k_i}_{M_i m_i \mu_i} C^{J_i l_i' k_i'}_{M_i m_i' \mu_i'} \begin{pmatrix} J_i & \lambda & J_i \\ -M_i & 0 & M_i \end{pmatrix} (-1)^{J_i - M_i - J_f + l_f} (-1)^{k_i + k_i' + k_f + k_f' + \mu_i} \times {\rm i}^{l_i - l_i'} Y^*_{l_i m_i}(\theta_v, \phi_v) Y_{l_i' m_i'}(\theta_v, \phi_v) \times (2J+1)(2J'+1) [(2\lambda+1)(2\lambda'+1)(2k_f+1)(2k_f'+1)]^{\frac{1}{2}} \times \begin{pmatrix} k_i' & k_i & \lambda' \\ -\mu_i' & \mu_i & 0 \end{pmatrix} \begin{Bmatrix} k_i' & k_i & \lambda' \\ J & J' & s \end{Bmatrix} \begin{Bmatrix} k_f' & k_f & \lambda' \\ J & J' & s \end{Bmatrix} \begin{Bmatrix} k_f & k_f' & \lambda' \\ J_f & J_f & l_f \end{Bmatrix} \times \langle \alpha_i J_i l_i k_i s J | T | \alpha_f J_f l_f k_f s J \rangle \langle \alpha_i J_i l_i' k_i' s J' | T | \alpha_f J_f l_f k_f' s J' \rangle^*. \qquad (61)$$

The tensorial cross section is defined by (31) and so using (A.7) and (A.8) the final sums over the magnetic quantum numbers in (61) are carried out and we obtain the following explicit general expression for the tensorial cross section:

$$
\begin{aligned}
{}^{\kappa}\sigma_{\mathrm{trn}}^{\lambda\lambda'}(\alpha_i J_i \rightarrow \alpha_f J_f; v) &= \pi \left(\frac{\hbar}{\mathcal{M}v}\right)^2 \frac{1}{(2s+1)} [(2\lambda+1)(2\lambda'+1)]^{\frac{1}{2}} \begin{pmatrix} \lambda & \lambda' & \kappa \\ 0 & 0 & 0 \end{pmatrix} \\
&\times \sum_{JJ'} \sum_{l_i l_i' l_f} \sum_{k_i k_i' k_f k_f'} \mathrm{i}^{l_i - l_i'} (2J+1)(2J'+1)(-1)^{J_f + l_i' + l_f + k_i' + k_f' - k_f} \\
&\times [(2k_i+1)(2k_i'+1)(2k_f+1)(2k_f'+1)(2l_i+1)(2l_i'+1)]^{\frac{1}{2}} \\
&\times \begin{pmatrix} l_i & l_i' & \kappa \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} k_f' & k_f & \lambda' \\ J_f & J_f & l_f \end{Bmatrix} \begin{Bmatrix} k_i' & k_i & \lambda' \\ J & J' & s \end{Bmatrix} \begin{Bmatrix} k_f' & k_f & \lambda' \\ J & J' & s \end{Bmatrix} \begin{Bmatrix} J_i & k_i & l_i \\ J_i & k_i' & l_i' \\ \lambda & \lambda' & \kappa \end{Bmatrix} \\
&\times \langle \alpha_i J_i l_i k_i s J | T | \alpha_f J_f l_f k_f s J \rangle \langle \alpha_i J_i l_i' k_i' s J' | T | \alpha_f J_f l_f k_f' s J' \rangle^*. \qquad (62)
\end{aligned}
$$

Note that since κ is always even, $l_i - l_i'$ is even and hence the expression given in (62) is real.

6.2. Collisional relaxation

The statistical equilibrium equations (16) include the probability of relaxation processes $\mathcal{P}(f \rightarrow f)$ taking place and we now consider the collisional depopulation of a level i caused by a transition $i \rightarrow f$. The collisional relaxation cross section can be written as

$$
\sigma_{\mathrm{rel}}(\alpha_i J_i M_i \rightarrow \alpha_f J_f; \boldsymbol{v}) = \sum_{M_f} \sigma_{\mathrm{trn}}(\alpha_i J_i M_i \rightarrow \alpha_f J_f M_f; \boldsymbol{v}) \qquad (63)
$$

and so using equation (A.2) we evaluate successively the sums over $M_f m_f$, $\mu_f m_s'$ and $M m_s$ in (58) and (59) to obtain

$$
\begin{aligned}
\sigma_{\mathrm{rel}}(\alpha_i J_i M_i \rightarrow \alpha_f J_f; \boldsymbol{v}) &= \left(\frac{2\pi\hbar}{\mathcal{M}v}\right)^2 \frac{1}{(2s+1)} \sum_{J l_i l_i' l_f k_i k_f} \sum_{m_i m_i' \mu_i} \frac{(2J+1)}{(2k_i+1)} \\
&\times C^{J_i l_i k_i}_{M_i m_i \mu_i} C^{J_i l_i' k_i}_{M_i m_i' \mu_i} \mathrm{i}^{l_i - l_i'} Y^*_{l_i m_i}(\theta_v, \phi_v) Y_{l_i' m_i'}(\theta_v, \phi_v) \\
&\times \langle \alpha_i J_i l_i k_i s J | T | \alpha_f J_f l_f k_f s J \rangle \langle \alpha_i J_i l_i' k_i s J | T | \alpha_f J_f l_f k_f s J \rangle^*. \qquad (64)
\end{aligned}
$$

For relaxation processes a multipolar expansion of the cross section is defined by, see (29),

$$
\begin{aligned}
\sigma_{\mathrm{rel}}^{\lambda\lambda'}(\alpha_i J_i \rightarrow \alpha_f J_f; \boldsymbol{v}) &= \sum_{M_i} [(2\lambda+1)(2\lambda'+1)]^{\frac{1}{2}} \begin{pmatrix} J_i & \lambda & J_i \\ -M_i & 0 & M_i \end{pmatrix} \begin{pmatrix} J_i & \lambda' & J_i \\ -M_i & 0 & M_i \end{pmatrix} \\
&\times \sigma_{\mathrm{rel}}(\alpha_i J_i M_i \rightarrow \alpha_f J_f; \boldsymbol{v}). \qquad (65)
\end{aligned}
$$

Then introducing the tensorial cross section (31) and using (A.7), we obtain

$$
\begin{aligned}
{}^{\kappa}\sigma_{\mathrm{rel}}^{\lambda\lambda'}(\alpha_i J_i \rightarrow \alpha_f J_f; v) &= \pi \left(\frac{\hbar}{\mathcal{M}v}\right)^2 \frac{1}{(2s+1)} [(2\lambda+1)(2\lambda'+1)]^{\frac{1}{2}} \\
&\times \sum_{J l_i l_i' l_f k_i k_f} \frac{(2J+1)}{(2k_i+1)} [(2l_i+1)(2l_i'+1)]^{\frac{1}{2}} \begin{pmatrix} l_i & l_i' & \kappa \\ 0 & 0 & 0 \end{pmatrix} \mathrm{i}^{l_i - l_i'} \\
&\times \langle \alpha_i J_i l_i k_i s J | T | \alpha_f J_f l_f k_f s J \rangle \langle \alpha_i J_i l_i' k_i s J | T | \alpha_f J_f l_f k_f s J \rangle^* \\
&\times \sum_{M_i m_i \mu_i} (-1)^{m_i} C^{J_i l_i k_i}_{M_i m_i \mu_i} C^{J_i l_i' k_i}_{M_i m_i' \mu_i} \\
&\times \begin{pmatrix} J_i & \lambda & J_i \\ -M_i & 0 & M_i \end{pmatrix} \begin{pmatrix} J_i & \lambda' & J_i \\ -M_i & 0 & M_i \end{pmatrix} \begin{pmatrix} l_i & l_i' & \kappa \\ -m_i & m_i & 0 \end{pmatrix}. \qquad (66)
\end{aligned}
$$

The sums over $m_i\mu_i$ and M_i in (66) are carried out using (A.6) and then finally

$$
\begin{aligned}
{}^{\kappa}\sigma_{\mathrm{rel}}^{\lambda\lambda'}(\alpha_i J_i \to \alpha_f J_f; v) &= \pi\left(\frac{\hbar}{\mathcal{M}v}\right)^2 \frac{1}{(2s+1)}[(2\lambda+1)(2\lambda'+1)]^{\frac{1}{2}} \\
&\times \begin{pmatrix} \lambda & \lambda' & \kappa \\ 0 & 0 & 0 \end{pmatrix} \sum_{J l_i l_i' l_f k_i k_f} \mathrm{i}^{l_i - l_i'}(2J+1)[(2l_i+1)(2l_i'+1)]^{\frac{1}{2}}(-1)^{J_i - k_i} \\
&\times \begin{pmatrix} l_i & l_i' & \kappa \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} \lambda & \lambda' & \kappa \\ J_i & J_i & J_i \end{Bmatrix} \begin{Bmatrix} l_i & l_i' & \kappa \\ J_i & J_i & k_i \end{Bmatrix} \\
&\times \langle \alpha_i J_i l_i k_i s J | T | \alpha_f J_f l_f k_f s J\rangle \langle \alpha_i J_i l_i' k_i s J | T | \alpha_f J_f l_f k_f s J\rangle^{*}. \qquad (67)
\end{aligned}
$$

7. Tensorial radiative rates

7.1. Absorption and stimulated emission

From equations (20), (38) and (39), we obtain

$$
B(\alpha_i J_i M_i \to \alpha_f J_f M_f; \hat{\boldsymbol{k}}) = \frac{3}{4\pi}(2J_i+1)B(\alpha_i J_i \to \alpha_f J_f)\mathcal{T}(J_i, J_f, 1; \hat{\boldsymbol{k}}) \qquad (68)
$$

and using definition (29)

$$
\begin{aligned}
B_{\mathrm{trn}}^{\lambda\lambda'}(\alpha_i J_i \to \alpha_f J_f; \hat{\boldsymbol{k}}) &= \sum_{M_i M_f} (-1)^{J_i - M_i + J_f - M_f}[(2\lambda+1)(2\lambda'+1)]^{\frac{1}{2}} \\
&\times \begin{pmatrix} J_i & \lambda & J_i \\ -M_i & 0 & M_i \end{pmatrix} \begin{pmatrix} J_f & \lambda' & J_f \\ -M_f & 0 & M_f \end{pmatrix} B(\alpha_i J_i M_i \to \alpha_f J_f M_f; \hat{\boldsymbol{k}}). \qquad (69)
\end{aligned}
$$

On combining equations (68) and (69), we use (A.8) to carry out the sums over the magnetic quantum numbers and so

$$
\begin{aligned}
B_{\mathrm{trn}}^{\lambda\lambda'}(\alpha_i J_i \to \alpha_f J_f; \hat{\boldsymbol{k}}) &= \frac{3}{4\pi}(2J_i+1)B(\alpha_i J_i \to \alpha_f J_f)\sum_l (2l+1)\begin{pmatrix} 1 & 1 & l \\ -1 & 1 & 0 \end{pmatrix}\begin{pmatrix} \lambda & \lambda' & l \\ 0 & 0 & 0 \end{pmatrix} \\
&\times [(2\lambda+1)(2\lambda'+1)]^{\frac{1}{2}}(-1)^{\lambda'}\begin{Bmatrix} J_i & J_f & 1 \\ J_i & J_f & 1 \\ \lambda & \lambda' & l \end{Bmatrix}\mathcal{D}_{00}^{(l)*}(\hat{\boldsymbol{k}}). \qquad (70)
\end{aligned}
$$

Then it follows directly from (34) and (A.5) that

$$
\begin{aligned}
{}^{\kappa}B_{\mathrm{trn}}^{\lambda\lambda'}(\alpha_i J_i \to \alpha_f J_f) &= 3(2J_i+1)B(\alpha_i J_i \to \alpha_f J_f)\begin{pmatrix} 1 & 1 & \kappa \\ -1 & 1 & 0 \end{pmatrix}\begin{pmatrix} \lambda & \lambda' & \kappa \\ 0 & 0 & 0 \end{pmatrix} \\
&\times [(2\lambda+1)(2\lambda'+1)]^{\frac{1}{2}}(-1)^{\lambda'}\begin{Bmatrix} J_i & J_f & 1 \\ J_i & J_f & 1 \\ \lambda & \lambda' & \kappa \end{Bmatrix}. \qquad (71)
\end{aligned}
$$

7.2. Radiative relaxation

The multipole coefficients for radiative relaxation are defined by

$$
\begin{aligned}
B_{\mathrm{rel}}^{\lambda\lambda'}(\alpha_i J_i \to \alpha_f J_f; \hat{\boldsymbol{k}}) &= \sum_{M_i M_f}[(2\lambda+1)(2\lambda'+1)]^{\frac{1}{2}} \\
&\times \begin{pmatrix} J_i & \lambda & J_i \\ -M_i & 0 & M_i \end{pmatrix}\begin{pmatrix} J_i & \lambda' & J_i \\ -M_i & 0 & M_i \end{pmatrix} B(\alpha_i J_i M_i \to \alpha_f J_f M_f; \hat{\boldsymbol{k}}), \qquad (72)
\end{aligned}
$$

cf (65) and (69). By combining (68) and (72), the sums over μ' and M_f followed by the sum over M_i can be evaluated using (A.6) to give

$$B_{\text{rel}}^{\lambda\lambda'}(\alpha_i J_i \to \alpha_f J_f; \hat{\boldsymbol{k}}) = \frac{3}{4\pi}(2J_i+1)B(\alpha_i J_i \to \alpha_f J_f)\sum_l (2l+1)\begin{pmatrix} 1 & 1 & l \\ -1 & 1 & 0 \end{pmatrix}\begin{pmatrix} \lambda & \lambda' & l \\ 0 & 0 & 0 \end{pmatrix}$$
$$\times [(2\lambda+1)(2\lambda'+1)]^{\frac{1}{2}}(-1)^{J_i-J_f+1}\begin{Bmatrix} J_i & J_i & l \\ 1 & 1 & J_f \end{Bmatrix}\begin{Bmatrix} \lambda & \lambda' & l \\ J_i & J_i & J_i \end{Bmatrix}\mathcal{D}_{00}^{(l)*}(\hat{\boldsymbol{k}}). \qquad (73)$$

Then as above it follows that

$$^{\kappa}B_{\text{rel}}^{\lambda\lambda'}(\alpha_i J_i \to \alpha_f J_f) = 3(2J_i+1)B(\alpha_i J_i \to \alpha_f J_f)\begin{pmatrix} 1 & 1 & \kappa \\ -1 & 1 & 0 \end{pmatrix}\begin{pmatrix} \lambda & \lambda' & \kappa \\ 0 & 0 & 0 \end{pmatrix}$$
$$\times [(2\lambda+1)(2\lambda'+1)]^{\frac{1}{2}}(-1)^{J_i-J_f+1}\begin{Bmatrix} \lambda & \lambda' & \kappa \\ J_i & J_i & J_i \end{Bmatrix}\begin{Bmatrix} J_i & J_i & \kappa \\ 1 & 1 & J_f \end{Bmatrix}. \qquad (74)$$

Results (71) and (74) agree with those given by Vogt *et al* [18].

7.3. Spontaneous emission

The rate for spontaneous emission is given by the Einstein A coefficient, see (40). We merely note that by setting $\kappa = 0$ and $\lambda = \lambda'$ in (74), and using (A.9) and (A.10), we obtain

$$^{0}B_{\text{rel}}^{\lambda\lambda}(\alpha_i J_i \to \alpha_f J_f) = 3(2J_i+1)B(\alpha_i J_i \to \alpha_f J_f)\begin{pmatrix} 1 & 1 & 0 \\ -1 & 1 & 0 \end{pmatrix}\begin{pmatrix} \lambda & \lambda & 0 \\ 0 & 0 & 0 \end{pmatrix}$$
$$\times (2\lambda+1)(-1)^{J_i-J_f+1}\begin{Bmatrix} \lambda & \lambda & 0 \\ J_i & J_i & J_i \end{Bmatrix}\begin{Bmatrix} J_i & J_i & 0 \\ 1 & 1 & J_f \end{Bmatrix}$$
$$= \frac{c^2}{2h\nu^3}A(\alpha_i J_i \to \alpha_f J_f), \qquad (75)$$

as expected.

8. Tensorial collision cross sections: special cases

8.1. Excitation by spinless particles

The expression for the tensorial cross section in (66) simplifies for $s = 0$ since then $k_i = k_f = J$ and $k_i' = k_f' = J'$ and so on using (A.10) and the symmetry properties of the $6j$ and $9j$ symbols we obtain

$$^{\kappa}\sigma_{\text{trn}}^{\lambda\lambda'}(\alpha_i J_i \to \alpha_f J_f; v) = \pi\left(\frac{\hbar}{\mathcal{M}v}\right)^2[(2\lambda+1)(2\lambda'+1)]^{\frac{1}{2}}\begin{pmatrix} \lambda & \lambda' & \kappa \\ 0 & 0 & 0 \end{pmatrix}$$
$$\times \sum_{JJ'}\sum_{l_i l_i' l_f} \mathrm{i}^{l_i-l_i'}(2J+1)(2J'+1)(-1)^{J_f+l_i'+l_f+J}$$
$$\times [(2l_i+1)(2l_i'+1)]^{\frac{1}{2}}\begin{pmatrix} l_i & l_i' & \kappa \\ 0 & 0 & 0 \end{pmatrix}\begin{Bmatrix} J & J' & \lambda' \\ J_f & J_f & l_f \end{Bmatrix}\begin{Bmatrix} J_i & J & l_i \\ J_i & J' & l_i' \\ \lambda & \lambda' & \kappa \end{Bmatrix}$$
$$\times \langle \alpha_i J_i l_i J|T|\alpha_f J_f l_f J\rangle\langle \alpha_i J_i l_i' J'|T|\alpha_f J_f l_f J'\rangle^*. \qquad (76)$$

This expression agrees with that given by Follmeg *et al* [8] who consider collision-induced alignment in the system N_2^+–He.

8.2. LS coupling

Individual lines within a multiplet may not be distinguishable. If the plasma densities are such that the widths of the lines produced by pressure broadening are comparable with the fine structure splittings, then the components of the multiplet overlap and the problem is best formulated in LS coupling. This formulation was used in [15] and follows directly from the theory in [1]. However, in high-density plasmas, isotropic collisions with local particles may become non-negligible and then this depolarizing process can be taken into account in the solution of the statistical equilibrium equations. In the following discussion we consider plasmas for which this effect can be neglected.

In this section, we specify a state i of the target plus the colliding particle by the quantum numbers $L_i M_i S_i M_{S_i}$ and $l_i m_i s m_s$. The spins S_i and s couple to give the total spin S and then by replacing J_i, J_f, J and J' by L_i, L_f, L and L', respectively in (76) it follows that the tensorial excitation cross section in LS coupling is given by

$$
\begin{aligned}
{}^{\kappa}\sigma^{\lambda\lambda'}_{\text{trn}}(\alpha_i S_i L_i \rightarrow \alpha_f S_f L_f; v) &= \pi\left(\frac{\hbar}{\mathcal{M}v}\right)^2 [(2\lambda+1)(2\lambda'+1)^{\frac{1}{2}}\begin{pmatrix}\lambda & \lambda' & \kappa\\ 0 & 0 & 0\end{pmatrix}\\
&\times \sum_S \frac{(2S+1)}{(2s+1)(2S_i+1)} \sum_{LL'}\sum_{l_i l_i' l_f} \mathrm{i}^{l_i-l_i'}(2L+1)(2L'+1)(-1)^{L_f+l_i'+l_f+L}\\
&\times [(2l_i+1)(2l_i'+1)]^{\frac{1}{2}}\begin{pmatrix}l_i & l_i' & \kappa\\ 0 & 0 & 0\end{pmatrix}\begin{Bmatrix}L & L' & \lambda'\\ L_f & L_f & l_f\end{Bmatrix}\begin{Bmatrix}L_i & L & l_i\\ L_i & L' & l_i'\\ \lambda & \lambda' & \kappa\end{Bmatrix}\\
&\times \langle\alpha_i S_i L_i l_i SL|T|\alpha_f S_f L_f l_f SL\rangle\langle\alpha_i S_i L_i l_i' SL'|T|\alpha_f S_f L_f l_f SL'\rangle^*. \qquad (77)
\end{aligned}
$$

Similarly, we obtain the relaxation cross section from (67), i.e.

$$
\begin{aligned}
{}^{\kappa}\sigma^{\lambda\lambda'}_{\text{rel}}(\alpha_i S_i L_i \rightarrow \alpha_f S_f L_f; v) &= \pi\left(\frac{\hbar}{\mathcal{M}v}\right)^2 [(2\lambda+1)(2\lambda'+1)]^{\frac{1}{2}}\begin{pmatrix}\lambda & \lambda' & \kappa\\ 0 & 0 & 0\end{pmatrix}\\
&\times \sum_S \frac{(2S+1)}{(2s+1)(2S_i+1)} \sum_{L l_i l_i' l_f} \mathrm{i}^{l_i-l_i'}(2L+1)[(2l_i+1)(2l_i'+1)]^{\frac{1}{2}}(-1)^{L_i-L}\\
&\times \begin{pmatrix}l_i & l_i' & \kappa\\ 0 & 0 & 0\end{pmatrix}\begin{Bmatrix}\lambda & \lambda' & \kappa\\ L_i & L_i & L_i\end{Bmatrix}\begin{Bmatrix}l_i & l_i' & \kappa\\ L_i & L_i & L\end{Bmatrix}\\
&\times \langle\alpha_i S_i L_i l_i SL|T|\alpha_f S_f L_f l_f SL\rangle\langle\alpha_i S_i L_i l_i' SL|T|\alpha_f S_f L_f l_f SL\rangle^*. \qquad (78)
\end{aligned}
$$

8.3. Equally populated substates

If the initial target state has equally populated substates, then $N_{\alpha_i J_i M_i} \equiv N_{\alpha_i J_i}/(2J_i+1)$, $\rho_0^{\lambda}(\alpha_i J_i)$ is given by (54) and from (A.9), (A.12) and (66) we have that

$$
\begin{aligned}
{}^{\kappa}\sigma^{0\kappa}_{\text{trn}}(\alpha_i J_i \rightarrow \alpha_f J_f; v) &= \pi\left(\frac{\hbar}{\mathcal{M}v}\right)^2 \frac{1}{(2s+1)}[(2\kappa+1)(2J_i+1)]^{-\frac{1}{2}}\\
&\times \sum_{JJ'}\sum_{l_i l_i' l_f}\sum_{k_i k_i' k_f k_f'} \mathrm{i}^{l_i-l_i'}(2J+1)(2J'+1)(-1)^{J_f-J_i+l_f+k_f'-k_f}\\
&\times [(2k_i+1)(2k_i'+1)(2k_f+1)(2k_f'+1)(2l_i+1)(2l_i'+1)]^{\frac{1}{2}}\\
&\times \begin{pmatrix}l_i & l_i' & \kappa\\ 0 & 0 & 0\end{pmatrix}\begin{Bmatrix}k_f' & k_f & \kappa\\ J_f & J_f & l_f\end{Bmatrix}\begin{Bmatrix}k_i' & k_i & \kappa\\ J & J' & s\end{Bmatrix}\begin{Bmatrix}k_f' & k_f & \kappa\\ J & J' & s\end{Bmatrix}\begin{Bmatrix}l_i & l_i' & \kappa\\ k_i' & k_i & J_i\end{Bmatrix}\\
&\times \langle\alpha_i J_i l_i k_i sJ|T|\alpha_f J_f l_f k_f sJ\rangle\langle\alpha_i J_i l_i' k_i' sJ'|T|\alpha_f J_f l_f k_f' sJ'\rangle^*. \qquad (79)
\end{aligned}
$$

Also if in addition, the final state $\alpha_f J_f$ is also equally populated, then we only need the case $\kappa = 0$ in (79), which reduces to

$$
\begin{aligned}
{}^0\sigma^{00}_{\mathrm{trn}}(\alpha_i J_i \to \alpha_f J_f; v) &= \pi \left(\frac{\hbar}{\mathcal{M}v}\right)^2 \frac{1}{(2s+1)} [(2J_i+1)(2J_f+1)]^{-\frac{1}{2}} \\
&\quad \times \sum_{l_i l_f k_i k_f J} (2J+1) |\langle \alpha_i J_i l_i k_i s J | T | \alpha_f J_f l_f k_f s J \rangle|^2 \\
&= \left(\frac{2J_i+1}{2J_f+1}\right)^{\frac{1}{2}} Q(\alpha_i J_i \to \alpha_f J_f; v),
\end{aligned} \tag{80}
$$

where $Q(\alpha_i J_i \to \alpha_f J_f; v)$ is the usual collision cross section for a transition $\alpha_i J_i \to \alpha_f J_f$, cf [29].

8.4. Monoenergetic particle beams

In laboratory collision experiments the target system is prepared in an initial state $\alpha_g J_g$ and the system is excited by collisions to a state $\alpha_i J_i$ using a monoenergetic beam of particles. The polarization of the radiation emitted in a transition $\alpha_i J_i \to \alpha_f J_f$ is then observed, cf Andersen and Bartschat [3]. If v_z is the velocity of the particle beam along the axis Oz, by setting $\cos\theta_v = 1$ in (32) it follows that

$$
\sigma^{\lambda\lambda'}_{\mathrm{trn}}(\alpha_g J_g \to \alpha_i J_i; v_z) = \sum_\kappa (2\kappa+1)\, {}^\kappa\sigma^{\lambda\lambda'}_{\mathrm{trn}}(\alpha_g J_g \to \alpha_i J_i; v_z). \tag{81}
$$

If we assume that initially the target system occupies a single state $\alpha_g J_g$ which is unpolarized, i.e. the substates are equally populated, then (48), (53) and (54) give

$$
\frac{\rho^2_0(\alpha_i J_i)}{\rho^0_0(\alpha_i J_i)} = \frac{C^{02}_{\mathrm{trn}}(\alpha_g J_g \to \alpha_i J_i; v_z)}{C^{00}_{\mathrm{trn}}(\alpha_g J_g \to \alpha_i J_i; v_z)} = \frac{\sigma^{02}_{\mathrm{trn}}(\alpha_g J_g \to \alpha_i J_i; v_z)}{\sigma^{00}_{\mathrm{trn}}(\alpha_g J_g \to \alpha_i J_i; v_z)}. \tag{82}
$$

9. Radiative transitions: special cases

Throughout this section we assume that only collisional excitation and spontaneous emission processes are important so that the statistical equilibrium equations reduce to the form (53). Explicit values for the coefficients $\Omega_\lambda(J' \to J)$ required, see (46), can easily be obtained from (A.10) and (A.11).

9.1. Transitions in hydrogen

We first consider the Lyman series in hydrogen where the hydrogen atom is initially in the ground state. Excitation by collisions populates the nl states and then the radiation emitted in the transition $n\mathrm{p} \to 1\mathrm{s}$ is observed. This gives direct experimental information about the collisional excitation of the $n\mathrm{p}$ state. If we assume LS coupling, then using (44), (54) and (A.10), we obtain the simple result

$$
\eta = \frac{1}{2\sqrt{2}} \frac{\begin{Bmatrix} 1 & 1 & 2 \\ 1 & 1 & 0 \end{Bmatrix}}{\begin{Bmatrix} 1 & 1 & 0 \\ 1 & 1 & 0 \end{Bmatrix}} \frac{\rho^2_0(n\mathrm{p}\,^2\mathrm{P})}{\rho^0_0(n\mathrm{p}\,^2\mathrm{P})} = \frac{1}{2\sqrt{2}} \frac{C^{02}_{\mathrm{trn}}(1\mathrm{s}\,^2\mathrm{S} \to n\mathrm{p}\,^2\mathrm{P})}{C^{00}_{\mathrm{trn}}(1\mathrm{s}\,^2\mathrm{S} \to n\mathrm{p}\,^2\mathrm{P})}, \tag{83}
$$

so that the degree of linear polarization is directly related to the ratio of collisional alignment to collisional population transfer. If the fine structure of the $n\mathrm{p}^2\mathrm{P}$ state is taken into account, then only one component of the line is polarized. In this case (83) is replaced by

$$\eta = \frac{1}{2\sqrt{2}} \frac{\Omega_2\big(\frac{3}{2} \to \frac{1}{2}\big) A\big(n\mathrm{p}^2\mathrm{P}_{\frac{3}{2}} \to 1\mathrm{s}^2\mathrm{S}_{\frac{1}{2}}\big)\, \rho_0^2\big(n\mathrm{p}^2\mathrm{P}_{\frac{3}{2}}\big)}{\sum_{J=\frac{1}{2},\frac{3}{2}} \Omega_0\big(J \to \frac{1}{2}\big) A\big(n\mathrm{p}^2\mathrm{P}_J \to 1\mathrm{s}^2\mathrm{S}_{\frac{1}{2}}\big) \rho_0^0(n\mathrm{p}^2\mathrm{P}_J)} \tag{84}$$

on using (45) and (46) and where the density matrix elements ρ_0^λ are given by (53).

Secondly, we consider H_α radiation. Collisions populate the degenerate states 3s, 3p and 3d and then radiation is emitted in transitions to the 2s and 2p levels. If we assume LS coupling in (45), the expression for $\Omega_\lambda(J_i \to J_f)$ in (46) shows that two of the three components, $3\mathrm{p} \to 2\mathrm{s}$ and $3\mathrm{d} \to 2\mathrm{p}$, are polarized. However, when fine structure is included, there are seven components, $3\mathrm{s}_{\frac{1}{2}} \to 2\mathrm{p}_{\frac{1}{2},\frac{3}{2}}$, $3\mathrm{p}_{\frac{1}{2}} \to 2\mathrm{s}_{\frac{1}{2}}$, $3\mathrm{p}_{\frac{3}{2}} \to 2\mathrm{s}_{\frac{1}{2}}$, $3\mathrm{d}_{\frac{3}{2}} \to 2\mathrm{p}_{\frac{1}{2},\frac{3}{2}}$ and $3\mathrm{d}_{\frac{5}{2}} \to 2\mathrm{p}_{\frac{3}{2}}$, of which the first three are unpolarized.

9.2. Transitions in helium

We assume that initially excited states $n'l'$ of helium are populated by collisional excitation from the ground state. It is clear that for singlet transitions of the type $n'\mathrm{p}^1\mathrm{P}_1 \to n\mathrm{s}^1\mathrm{S}_0$, both LS coupling and the inclusion of fine structure give the same result, i.e.

$$\eta = \frac{1}{2\sqrt{2}} \frac{C_{\mathrm{trn}}^{02}(1\mathrm{s}^2\,{}^1\mathrm{S} \to 1\mathrm{s}n\mathrm{p}^1\mathrm{P})}{C_{\mathrm{trn}}^{00}(1\mathrm{s}^2\,{}^1\mathrm{S} \to 1\mathrm{s}n\mathrm{p}^1\mathrm{P})}, \tag{85}$$

cf (83). For triplet transitions $n'\mathrm{p}^3\mathrm{P}_{0,1,2} \to n\mathrm{s}^3\mathrm{S}_1$, LS coupling again gives a result similar to (85) and in this case if the colliding particles are electrons, then collisional excitation from the ground state can only occur through electron exchange. When allowance for fine structure is made in (45), only two components, $n'\mathrm{p}^3\mathrm{P}_{1,2} \to n\mathrm{s}^3\mathrm{S}_1$, of the line are polarized, which decreases significantly the total polarization achieved.

As a final example, we consider transitions $1\mathrm{s}n'\mathrm{d}^3\mathrm{D}_{J'} \to 1\mathrm{s}n\mathrm{p}^3\mathrm{P}_J$ in helium. For the case of LS coupling, we set $J_i = L_i = 2$ and $J_f = L_f = 1$ in (46) and then (45) and (82) give

$$\eta = \frac{1}{2\sqrt{2}} \frac{\Omega_2(2 \to 1)}{\Omega_0(2 \to 1)} \frac{{}^2\sigma_{\mathrm{trn}}^{02}(1\mathrm{s}^2\,{}^1\mathrm{S} \to 1\mathrm{s}n'\mathrm{d}^3\mathrm{D})}{{}^2\sigma_{\mathrm{trn}}^{00}(1\mathrm{s}^2\,{}^1\mathrm{S} \to 1\mathrm{s}n'\mathrm{d}^3\mathrm{D})}. \tag{86}$$

Allowance for fine structure splitting gives rise to six components, $1\mathrm{s}n'\mathrm{d}^3\mathrm{D}_1 \to 1\mathrm{s}n\mathrm{p}^3\mathrm{P}_{0,1,2}$, $1\mathrm{s}n'\mathrm{d}^3\mathrm{D}_2 \to 1\mathrm{s}n\mathrm{p}^3\mathrm{P}_{1,2}$ and $1\mathrm{s}n'\mathrm{d}^3\mathrm{D}_3 \to 1\mathrm{s}n\mathrm{p}^3\mathrm{P}_2$, all of which contribute to the polarization of the line.

10. Conclusions

A comprehensive description has been presented of all the formulae required for a complete solution of the statistical equilibrium equations using both pair-coupling and LS-coupling schemes to describe the structure of the target system. The target is subjected to collisions with particles that have an anisotropic velocity distribution with cylindrical symmetry and the theory allows for the presence of an external radiation field. The consequent polarization of emission lines produced by radiative decay through allowed transitions can then be obtained. The theory has many applications to the analysis of spectra and is particularly important for the diagnostics of astrophysical and fusion plasmas. The theory can be easily specialized to the case where the colliding particles form a monoenergetic beam and there is no external radiation field. This then gives the appropriate form required for the interpretation of polarization and alignment in atomic and molecular collisions.

Acknowledgments

The support of the Observatoire de Paris during several visits to the Observatory by HES and GP is gratefully acknowledged. We are also indebted to Dr Sylvie Sahal–Bréchot for some interesting comments and to the referee for a careful reading of the manuscript.

Appendix

The book on angular momentum by Edmonds [31] is the basic reference for the notation and equation numbers quoted below. From equation (3.7.3) we have that

$$C^{j_1 j_2 j_3}_{m_1 m_2 m_3} = (-1)^{j_1-j_2+m_3}(2j_3+1)^{\frac{1}{2}} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & -m_3 \end{pmatrix} \tag{A.1}$$

where C^{abc}_{def} and $\left(\begin{smallmatrix} a & b & c \\ d & e & f \end{smallmatrix}\right)$ denote Clebsch–Gordan and $3j$ coefficients, respectively. The $3j$ coefficients obey the sum rule

$$\sum_{m_1 m_2} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \begin{pmatrix} j_1 & j_2 & j_3' \\ m_1 & m_2 & m_3' \end{pmatrix} = (2j_3+1)^{-1}\, \delta_{j_3 j_3'}\, \delta_{m_3 m_3'}, \tag{A.2}$$

see (3.7.8).

The Wigner–Eckhart theorem, see (5.4.1), defines the reduced matrix elements $\langle j' \| \mathbf{T}(k) \| j \rangle$ using the relation

$$\langle j'm' | T(k\ q) | jm \rangle = (-1)^{j'-m'} \begin{pmatrix} j' & k & j \\ -m' & q & m \end{pmatrix} \langle j' \| \boldsymbol{T}(k) \| j \rangle. \tag{A.3}$$

Matrix elements of the rotation operator $\mathcal{D}(\hat{\boldsymbol{k}})$ satisfy the relations

$$\begin{aligned} \mathcal{D}^{(j_1)*}_{m_1' m_1}(\hat{\boldsymbol{k}}) \mathcal{D}^{(j_2)}_{m_2' m_2}(\hat{\boldsymbol{k}}) &= (-1)^{m_1'-m_1} \sum_{j m' m} (2j+1) \\ &\times \begin{pmatrix} j_1 & j_2 & j \\ -m_1' & m_2' & m' \end{pmatrix} \mathcal{D}^{(j)*}_{m' m}(\hat{\boldsymbol{k}}) \begin{pmatrix} j_1 & j_2 & j \\ -m_1 & m_2 & m \end{pmatrix}, \end{aligned} \tag{A.4}$$

see (4.2.7) and (4.3.2), and

$$\begin{aligned} \mathcal{D}^{(l)}_{0m}(\hat{\boldsymbol{k}}) &= \left(\frac{4\pi}{2l+1} \right)^{\frac{1}{2}} Y_{lm}(\hat{\boldsymbol{k}}) \\ &= (-1)^m \left[\frac{(l-m)!}{(l+m)!} \right]^{\frac{1}{2}} P_l^m(\cos\theta_k) \exp(\mathrm{i} m \phi_k), \end{aligned} \tag{A.5}$$

see (2.5.29) and (4.1.25). In (A.5), $Y_{lm}(\hat{\boldsymbol{k}})$ is a normalized spherical harmonic and $P_l^m(\cos\theta_k)$ is the corresponding associated Legendre polynomial.

From equation (6.2.8), the $6j$ coefficients $\left\{\begin{smallmatrix} a & b & c \\ d & e & f \end{smallmatrix}\right\}$ are related to $3j$ coefficients by

$$\begin{aligned} \sum_{\mu_1 \mu_2 \mu_3} (-1)^{l_1+l_2+l_3+\mu_1+\mu_2+\mu_3} \begin{pmatrix} j_1 & l_2 & l_3 \\ m_1 & \mu_2 & -\mu_3 \end{pmatrix} \begin{pmatrix} l_1 & j_2 & l_3 \\ -\mu_1 & m_2 & \mu_3 \end{pmatrix} \begin{pmatrix} l_1 & l_2 & j_3 \\ \mu_1 & -\mu_2 & m_3 \end{pmatrix} \\ = \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \begin{Bmatrix} j_1 & j_2 & j_3 \\ l_1 & l_2 & l_3 \end{Bmatrix} \end{aligned} \tag{A.6}$$

and equations (2.5.6), (2.5.30) and (4.6.3) give the result

$$\int Y^*_{l_1m_1}(\theta,\phi)P_{l_2}(\cos\theta)Y_{l_3m_3}(\theta,\phi)\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi$$

$$= (-1)^{m_1}[(2l_1+1)(2l_3+1)]^{\frac{1}{2}}\begin{pmatrix} l_1 & l_2 & l_3 \\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix} l_1 & l_2 & l_3 \\ -m_1 & 0 & m_3\end{pmatrix}. \qquad \text{(A.7)}$$

Finally we also require a result, see Messiah [24], equation (C40.c), that relates the $9j$ coefficients $\begin{Bmatrix} a & b & c \\ d & e & f \\ g & h & i\end{Bmatrix}$ to $3j$ coefficients by

$$\sum_{m_{11}m_{12}m_{13}}\sum_{m_{21}m_{22}m_{23}}\begin{pmatrix} j_{11} & j_{12} & j_{13} \\ m_{11} & m_{12} & m_{13}\end{pmatrix}\begin{pmatrix} j_{21} & j_{22} & j_{23} \\ m_{21} & m_{22} & m_{23}\end{pmatrix}$$

$$\times\begin{pmatrix} j_{11} & j_{21} & j_{31} \\ m_{11} & m_{21} & m_{31}\end{pmatrix}\begin{pmatrix} j_{12} & j_{22} & j_{32} \\ m_{12} & m_{22} & m_{32}\end{pmatrix}\begin{pmatrix} j_{13} & j_{23} & j_{33} \\ m_{13} & m_{23} & m_{33}\end{pmatrix}$$

$$= \begin{pmatrix} j_{31} & j_{32} & j_{33} \\ m_{31} & m_{32} & m_{33}\end{pmatrix}\begin{Bmatrix} j_{11} & j_{12} & j_{13} \\ j_{21} & j_{22} & j_{23} \\ j_{31} & j_{32} & j_{33}\end{Bmatrix}. \qquad \text{(A.8)}$$

A few special cases of the coefficients listed above are also required. We have from equations (3.7.9), (6.3.2), (6.3.4), (6.4.14) and table 5 in [31] that

$$\begin{pmatrix} j_1 & j_2 & 0 \\ m_1 & m_2 & 0\end{pmatrix} = (-1)^{j_1-m_1}(2j_1+1)^{-\frac{1}{2}}\,\delta(j_1,j_2)\,\delta(m_1,-m_2), \qquad \text{(A.9)}$$

$$\begin{Bmatrix} j_1 & j_1 & 0 \\ 1 & 1 & j_2\end{Bmatrix} = (-1)^{j_1+j_2+1}[3(2j_1+1)]^{-\frac{1}{2}}, \qquad \text{(A.10)}$$

$$\begin{Bmatrix} j_1 & j_1 & 2 \\ 1 & 1 & j_2\end{Bmatrix} = (-1)^{j_1+j_2+1}\frac{2\,[3X(X-1)-8j_1(j_1+1)]}{[(2j_1-1)2j_1(2j_1+1)(2j_1+2)(2j_1+3)5!]^{\frac{1}{2}}},$$

$$X = (j_1-j_2)(j_1+j_2+1)+2, \qquad \text{(A.11)}$$

and

$$\begin{Bmatrix} j_{11} & j_{12} & j_{13} \\ j_{21} & j_{22} & j_{23} \\ j_{31} & j_{32} & 0\end{Bmatrix} = (-1)^{j_{12}+j_{21}+j_{13}+j_{31}}[(2j_{13}+1)(2j_{31}+1)]^{-\frac{1}{2}}\begin{Bmatrix} j_{11} & j_{12} & j_{13} \\ j_{22} & j_{21} & j_{31}\end{Bmatrix}$$

$$\times\,\delta(j_{13},j_{23})\,\delta(j_{31},j_{32}). \qquad \text{(A.12)}$$

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