ELECTRON IMPACT POLARIZATION OF ATOMIC SPECTRAL LINES. I.
A GENERAL THEORETICAL SCHEME

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ABSTRACT

A suitable theoretical scheme able to describe, in a wide variety of astrophysical situations, the phenomenon of atomic line polarization by electron impact is developed. Starting from the general principles of quantum mechanics and assuming the Born approximation, the rate equations for the density matrix elements of a multilevel atomic system, interacting with a nonrelativistic electron beam having any kind of angular distribution, are derived in full generality. The resulting theory generalizes the previous ones by accounting for the collisional rates and the cross sections concerning both inelastic and superelastic collisions (in any geometrical situation), and—moreover—by taking into account the coherences among Zeeman sublevels split by a magnetic field. The final equations for the collisional rates are made quite compact by the introduction of suitable spherical tensors connected with the components of the electric multipole moments of the atomic transitions.

As an example of particular relevance, the general formulae derived in the first sections of the paper are subsequently particularized to the case of the electric dipole interaction.

Subject headings: atomic processes — line: formation — polarization

1. INTRODUCTION

Polarization can originate in solar spectral lines by two different physical mechanisms: Zeeman splitting and atomic polarization. Zeeman splitting is due to the presence of a magnetic field in the line-forming layers; the resulting Zeeman effect induces linear and circular polarization across the profile of magnetically sensitive lines. Atomic polarization is a typical non-LTE effect consisting in (or phase relationships) between the sublevels themselves. Any anisotropy in the mechanism responsible for atomic excitation is the ultimate cause of atomic polarization and of the possible subsequent emission—by radiative de-excitation—of polarized radiation. For instance, polarization by resonance scattering occurring in the higher layers of the solar atmosphere and in the corona is induced by anisotropic illumination of the emitting atoms. Collisional excitation of atoms by particles with anisotropic velocity distributions is also another mechanism able to induce atomic polarization, which can then result in the emission of polarized line radiation. This latter process is called impact polarization.

This is the first in a planned series of papers concerned with developing a mathematical formalism able to describe electron impact polarization in a wide variety of astrophysical situations, coherently with the latest theoretical treatments of the generation and transfer of polarized radiation.

The presence, in flaring solar plasmas, of anisotropic velocity distributions of particles (electrons, protons) is suggested by various theoretical considerations. During a flare, the hard X-ray bursts are presumed to be produced by bremsstrahlung emission from electrons accelerated in the coronal regions of the flaring loop by an as yet ill-defined mechanism. Whether the nature of these electrons is "nonthermal" or "thermal" is a longstanding problem in the physics of solar flares which is still unsolved (for a recent review, see Dennis 1988 or Tandberg-Hanssen & Emslie 1988).

According to the nonthermal model, the accelerated electrons propagate along the magnetic lines in the form of highly anisotropic beams and interact with the ambient plasma in the legs of the loop ("thin target" emission) and at the footpoints ("thick target" emission). Besides radiation emission in the continuum, these suprathermal electrons are also responsible, by collisionally exciting atoms and ions, for line radiation emission. This line radiation should be partially polarized because of the anisotropy of the excitation mechanism. Detailed theoretical investigations indicate indeed that, in the nonthermal scenario, some impact polarization, \( P \), should be present in X-ray lines from hydrogen-like ions (\( P \approx 5\% \); Haug 1980), and from helium-like ions (\( P \approx 5\% - 15\% \); Shlyaptseva, Urnov, & Vinogradov 1981).

In the thermal model, the electrons responsible for bremsstrahlung have a relaxed, viz., Maxwellian, distribution. These electrons are part of a very hot plasma which initially is magnetically confined at the top of the flaring loop. Because of the heat diffusion, this energy release region spreads downward along the loop, between two conduction fronts which propagate symmetrically away from each other. Some of the high-energy electrons in the tail of the distribution can escape through these fronts and are guided by the magnetic field toward the footpoints, much as the electron beams in the nonthermal model. Here, according to both the thermal and...
the nonthermal model, the high-energy particles are thermalized: their energy is converted into heat in the denser plasma of the lower corona, transition region, and chromosphere. The resultant steep temperature gradient across these regions establishes a net heat flux directed along the solar vertical, toward the lower layers. The electron velocity distribution associated with this energy flux is non-Maxwellian. This introduces an anisotropy in the exciting mechanism (the collisions) of the emitting atoms. As a consequence, line radiation emitted by the transition region/chromospheric layers, where the conductive heat flux deposits its energy, is expected to exhibit some degree of impact polarization during a flare.

In the early 1980s, Hénoux et al. (1982) reported linearly polarized S I 1437 Å line emission during a solar flare. In this event the polarization of the emitted radiation was found to be directed toward disk center. The polarization of this chromospheric line was interpreted as impact polarization resulting from the line excitation by the abovementioned anisotropic distribution of energetic electrons associated with conductive heat flux (Hénoux et al. 1983). However, results from a more rigorous treatment of impact polarization originating from conductive heat flux in flaring plasmas (Fineschi et al. 1990a, b) show that the S I 1437 Å line is unlikely to be polarized up to the observed degree of few tens percent by electrons carrying heat flux. The reason is that the velocity distribution of this kind of electron has a significant departure from Maxwellian only for velocities greater than 3 times the electron thermal velocity. Therefore, in order to be appreciably polarized by electron impact from heat conduction, a given solar spectral line must have a threshold velocity larger than 3 times the electron thermal velocity of the plasma in which the line is formed. In this case, in fact, the atomic line excitation is predominantly due to the non-Maxwellian electrons in the anisotropic tail of the velocity distribution. The S I 1437 Å, however, is formed in a temperature range \((10^4 - 2 \times 10^4 \text{ K})\) in which the corresponding electron thermal velocity is lower than (or at most, equal to) 3 times the line threshold velocity. This, therefore, rules out impact by conductive electrons as the cause of the large polarization observed in that line. An additional result from the same treatment shows that electron impact polarization from heat conduction in solar flaring plasmas may be present in the neutral helium lines \(\lambda\lambda 522, 537,\) and 584. Also in this case, however, the degree of line polarization is unlikely to exceed few percent.

Recently, 100 keV proton beams bombarding the solar chromosphere and creating hot thermal plasma were proposed as an alternative explanation of the observed X-ray emission (Simnett 1986). Proton impact, indeed, has been invoked to account for some linear polarization detected in the Hα line (Hénoux et al. 1990). The observed polarization in the S I 1437 Å line might have the same origin as well (Martens & Young 1990). In order to assess the relative role played in solar flares by electron beams, electrons carrying heat flux, or neutral (electrons and protons) beams, further Hα measurements as well as observations in the extreme UV with new imaging polarimeters (Fineschi et al. 1991; Hoover et al. 1991) are highly welcome.

Besides direct electron bombardment and heat conduction, flare scenarios also include XUV irradiation among the ways of supplying energy to the chromosphere from the flaring corona. X-ray irradiation leads to populations of expelled electrons (the photo-electrons) which are superthermal—a few tens of eV—in comparison with the \(~ 1\text{ eV}\) background electrons. Theoretical considerations (Chame & Hénoux 1979) suggest that these photoelectrons—differently from particle beams and conductive heat—should be predominantly moving in the solar horizontal plane.

In this paper we develop a theoretical scheme able to describe the impact polarization of lines of neutral atoms excited by the type of anisotropic electrons mentioned in the discussion above (see Table I).

Although the general theoretical basis for describing line polarization in atomic collision processes is rather well understood and can be suitably derived within the framework of quantum mechanics, the specific theoretical treatment of impact polarization has been developed up to now mainly to explain experimental data and to make predictions for cases more pertaining to laboratory atomic spectroscopy than to astronomical spectroscopy. Therefore, since the formalism employed and the kind of physical approximations assumed differ from one field to another, this sometimes makes it difficult and awkward to carry useful results from one side to another and to establish connections between different aspects of the same problem. Moreover, there are particular situations of astrophysical interest—like, for instance, the presence of a magnetic field—that have not been considered before, except empirically (e.g., Skinner 1926).

For a review of experimental and theoretical results on impact polarization, the interested reader is referred to Kleinpoppen (1969). We limit ourselves to quote here a reduced list of papers which have contributed substantial results in the field. We will see in the following sections of this paper and in the subsequent papers of this series how all these results, and new original ones, can be obtained employing an unique and self-contained theoretical approach.

### Table 1

<table>
<thead>
<tr>
<th>KINETIC ENERGY OF THE ELECTRONS</th>
<th>TYPE OF ELECTRONS WITH NON-MAXWELLIAN VELOCITY DISTRIBUTION</th>
</tr>
</thead>
<tbody>
<tr>
<td>(-10^9) MeV</td>
<td>Relativistic electrons</td>
</tr>
<tr>
<td>(-10^8) keV</td>
<td>Electron beams impulsively accelerated during flares</td>
</tr>
<tr>
<td>(-10^7) keV</td>
<td>Nonrelativistic approximation limit</td>
</tr>
<tr>
<td>(-10^6) keV</td>
<td>Validity range of the present treatment</td>
</tr>
<tr>
<td>(-10^5) eV</td>
<td>Born approximation limit</td>
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<tr>
<td>(-10^4) eV</td>
<td>Photoelectrons produced via flaring XUV radiation</td>
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<tr>
<td>(-10^3) eV</td>
<td>Electrons carrying conductive heat flux</td>
</tr>
</tbody>
</table>

* Electron energy range that can be described through the present theory on impact polarization. The boundary constraints are given by the nonrelativistic approximation at high energies, and by the Born approximation at low energies. (The lower bound has been arbitrarily fixed around \(~ 10\text{ eV}\) having in mind the particular case of the Lyman z line.)
Impact polarization was discovered experimentally by Skinner (1926; see also Skinner & Appleyard 1928) and a first theoretical discussion was given by Oppenheimer (1928). A more complete theory was then developed by Percival & Seaton (1958). Both these treatments consider the case of dipole radiation emitted by an atom excited by a unidirectional electron beam. In the Oppenheimer theory allowance may be made for fine structure (FS) and hyperfine structure (HFS), but the theory is ambiguous when the FS or HFS are comparable with the natural line width. This theory, indeed, does not always satisfy the requirement of the principle of spectroscopic stability, namely the principle that the expressions for observed quantities derived from a quantum mechanical formalism should be independent of the choice of the representation. In Percival & Seaton’s theory, on the contrary, the expressions for the polarization can be given also when the FS or HFS separation is of the same order of magnitude as the natural width. The difference between the two theories is that, while in Oppenheimer’s treatment the photonic emission results from the sum of several independent contributions, each one due to the excitation of a single atomic level (sublevels), in the Percival & Seaton theory the same emission is described taking into account also the interferences among the single levels (sublevels). In both the theories the percentage polarization $P$ is finally expressed in terms of the cross sections $Q_{M_\ell}$ for excitation of quantum states with definite component $M_\ell$ of the orbital angular momentum, $L$—the quantization axis being in the direction of the incident electrons. The explicit expressions for $Q_{M_\ell}$ are thus derived in a frame of reference whose $z$-axis is parallel to the direction of the beam. In other words, given the atomic Hamiltonian $H_A$, the expressions of the cross sections $Q_{M_\ell}$ and thus of the observable $P$, are obtained using a quantum mechanical representation consisting of a complete set of eigenfunctions of the atomic Hamiltonian $H_A$ with the quantum numbers $M_\ell$ evaluated with respect to the incoming direction of the perturbing electron. This turns out to be a limitation if we want to take into account the presence of a magnetic field. In this case, in fact, the atomic Hamiltonian is conveniently diagonalized by choosing as quantization axis the magnetic field’s direction, which—in general—may not coincide with the direction of the incident electron. One of the objectives of this paper is to remove this limitation, deriving expressions for the cross sections and the collisional rates holding in any arbitrary coordinate frame.

A very general theory describing the various radiative mechanisms involved in the generation and transfer of polarized radiation has been presented by Landi Degl’Innocenti (1983; hereafter referred to as Paper I). The present paper employs a similar formalism and the relevant equations are derived according to the same perturbative scheme in the framework of quantum mechanics. For this reason the present paper can be considered as an extension of Paper I to the description of collisional mechanisms.

Section 2 is devoted to the introduction of the density-matrix formalism, to the discussion of some simplifying assumptions (impact approximation, nonrelativistic limit, spinless electrons, etc.), and to the formulation of the basic equations describing the time evolution of the atomic system according to the principles of quantum mechanics. In § 3 we derive the general expression of the statistical equilibrium equations for a multilevel atomic system collisionally interacting with an arbitrary distribution of electrons. These general equations are then particularized to the case of weak atom-electron interaction by introducing the Born approximation. The collisional electron-atom cross sections for any electric multipole transition are derived in § 4. In § 5 these cross sections, and the relative collisional rates, are written in an arbitrary coordinate frame. Finally, in the last section, we develop in more detail the relevant equations restricting ourselves to the case of the dipole approximation.

2. FORMULATION

We consider the interaction between a target atomic system and a colliding free electron. The total Hamiltonian of the coupled system can be written, in the Schrödinger picture, in the form

$$H = H_0 + V_S,$$

(2.1)

where $H_0$ is the unperturbed Hamiltonian which is the sum of the energies of the atomic system and of the free electron:

$$H_0 = H_A + H_{el},$$

(2.2)

while $V_S$ is the interaction Hamiltonian.

Let $S$ be the reference system whose origin coincides with the atomic nucleus, and whose $z$-axis is parallel to the trajectory of the free electron (Fig. 1). In such a coordinate system, the nonrelativistic expression of $V_S$ for a neutral atom is the following:

$$V_S = -\frac{Ze_0^2}{r_p} + \sum_{i=1}^{Z} e_0^2 \frac{r_i}{r_{pi}},$$

(2.3)

where $e_0$ is the electron charge, $r_p$ is the vector position of the colliding electron, $r_i (i = 1, 2, \ldots, Z)$ is the vector position of the $i$th optical electron, and $r_{pi} = r_p - r_i$.

We now assume the following simplifying hypothesis on the geometry of the collisional event:

$$r_p > r_i \quad i = 1, 2, \ldots, Z.\quad (2.4)$$

This is the so-called “long-range” approximation, and it allows us (through the introduction of the spherical coordinates defined in Fig. 1) to perform the following multipole expansion of the factor $1/r_{pi}$:

$$\frac{1}{r_{pi}} = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \frac{4\pi}{2l+1} \frac{\gamma}{r_p} Y_m(\theta_p, \varphi_p) Y_m(\theta_i, \varphi_i),$$

(2.5)

where $Y_m(\theta, \varphi)$ are the spherical harmonics, defined according to Schiff (1968):

$$Y_m(\theta, \varphi) = (-1)^{m+|m|} \frac{1}{4\pi} \left[ \frac{(2l+1)(l-|m|)!}{(l+|m|)!} \right]^{1/2} P_l^{|m|}(\cos \theta) e^{im\varphi},$$

(2.6)

with $P_l^{|m|}(\cos \theta)$ the associated Legendre function.
By means of the multipole expansion, the interaction Hamiltonian $V_s$ can be written in the form:

$$V_s = -\frac{Z e_0^2}{r_p} + \sum_{l=0}^{\infty} \sum_{m=-l}^{l} Q_{lm}(r_i) T_{lm}(r_p),$$

(2.7)

where $Q_{lm}(r_i)$, an operator acting only on the atomic variables, is defined by

$$Q_{lm}(r_i) = \left(\frac{4\pi}{2l+1}\right)^{1/2} \sum_{i=1}^{Z} r_i^l Y_{lm}^*(\theta_i, \varphi_i),$$

(2.8)

while $T_{lm}(r_p)$, an operator acting only on the free electron variables, is defined by

$$T_{lm}(r_p) = \left(\frac{4\pi}{2l+1}\right)^{1/2} \frac{e_0^2}{r_p^{l+1}} Y_{lm}(\theta_p, \varphi_p).$$

(2.9)

In expression (2.7) for $V_s$, the first term cancels out with the term $l = 0$ contained in the sum, so that equation (2.7) reduces to

$$V_s = \sum_{l=1}^{\infty} \sum_{m=-l}^{l} Q_{lm}(r_i) T_{lm}(r_p).$$

(2.10)

The interaction Hamiltonian can then be expressed in the interaction picture through the transformation

$$V_{it}(t) = \exp\left(2\pi i H_0 t/\hbar\right) V_s \exp\left(-2\pi i H_0 t/\hbar\right)$$

$$= \sum_{l=1}^{\infty} \sum_{m=-l}^{l} \exp(2\pi i H_A t/\hbar) Q_{lm}(r_i) \exp(-2\pi i H_A t/\hbar)$$

$$\times \left\{ \exp(2\pi i H_{el} t/\hbar) T_{lm}(r_p) \exp(-2\pi i H_{el} t/\hbar) \right\}.$$ 

(2.11)

This can be put in a more suitable form introducing both a complete set $\{|n_i\rangle\}$ of eigenvectors of the atomic Hamiltonian $H_A$:

$$H_A |n_i\rangle = E_n |n_i\rangle,$$

(2.12)

where $E_n$ is the energy eigenvalue corresponding to the eigenvector $|n_i\rangle$, and a complete set $\{|\psi\rangle\}$ of eigenvectors of the free electron Hamiltonian $H_{el}$:

$$H_{el} |\psi\rangle = E_{\psi} |\psi\rangle,$$

(2.13)

where, again, $E_{\psi}$ is the energy eigenvalue corresponding to the eigenvector $|\psi\rangle$. The eigenvectors $\{|\psi\rangle\}$ are characterized by the momentum of the free electron and by its spin projection. For the time being, with the symbol $\psi$ we mean the collection of the quantum numbers that characterize any single nondegenerate state of the free electron.

Both the sets of energy eigenvectors that we choose are orthonormal:

$$\langle x | n \rangle = \delta_{x n};$$

(2.14a)

$$\langle n | m \rangle = \delta_{nm},$$

(2.14b)
where $\delta$ is the Kronecker delta. Moreover, because of their completeness, these sets both obey the closure property:

$$\sum_{n} |n><n| = 1 ;$$  (2.15a)
$$\sum_{\psi} |\psi><\psi| = 1 .$$  (2.15b)

Introducing these last two relations into equation (2.11), at the left and at the right of each of the corresponding operators, we obtain:

$$V(t) = \sum_{l=1}^{\infty} \sum_{m=-l}^{l} \sum_{e,f} \sum_{\xi,x} [(Q_{e,f}(l, m)| e><f|)(T_{e,f}(l, m)| \xi><\xi|)] \exp [2\pi i (v_{e,f} + v_{\xi} t)] ,$$  (2.16)

where we have introduced the Bohr frequencies:

$$v_{e,f} = (E_{e} - E_{f})/h ,$$  (2.17a)
$$v_{\xi} = (E_{\xi} - E_{\eta})/h ,$$  (2.17b)

and the notations

$$q_{e,f}(l, m) = <e|Q_{mf}(l)| f> ,$$  (2.18a)
$$t_{e,f}(l, m) = <\xi|T_{mf}(l)| \xi> .$$  (2.18b)

After having expressed the interaction Hamiltonian in this form, we are in the position to deduce the time evolution of the physical quantities we are interested in. We describe the whole system by means of a density operator $\rho(t)$ expressed in the interaction picture. A given observable, $O(t)$, varies with time according to the following equation:

$$O(t) = Tr \{O(t)|\rho(t)|\} ,$$  (2.19)

where $\overline{O}(t)$ is the quantum operator which corresponds to the observable $O(t)$ expressed in the interaction picture, and where the symbol “$Tr$” means the trace operation.

Taking into account the Schrödinger equation for the density operator:

$$\frac{d\rho(t)}{dt} = -\frac{2\pi i}{\hbar} [V(t), \rho(t)] ,$$  (2.20)

where the symbol $[A, B]$ means the commutator $AB - BA$, the time evolution equation of $O(t)$ is given by (see Paper I, eqs. [25]-[29]):

$$\frac{dO(t)}{dt} = Tr \left\{ \frac{d\overline{O}(t)}{dt} \rho(t) \right\} - \frac{2\pi i}{\hbar} Tr \{[\overline{O}(t), V(t)]\rho(t)\}$$

$$- \frac{4\pi^2}{\hbar^2} Tr \left\{ \int_{0}^{t} [[\overline{O}(t), V(t')], V(t')] \rho(t')dt' \right\} ,$$  (2.21)

where $t = 0$ is the time corresponding to the beginning of the interaction. This is the exact equation which will be used in the following to deduce the statistical equilibrium equations for an atomic system interacting with an electronic beam. In the derivation we will, however, introduce some restrictive assumptions on the density operator that allow us to obtain a self-contained set of equations for the density-matrix elements of the atomic system.

The most relevant assumption is supposing that the $\rho_{s}$ operator for the whole system is the direct product of the single $\rho$-operators referring to the two interacting systems, or, with self-evident notation:

$$\rho_{s}(t') = \rho_{A}(t') \otimes \rho_{B}(t') \quad (0 \leq t' \leq t) .$$  (2.22)

If $A$ is an operator which acts only on the atomic variables, and $B$ is an operator which acts only on the free electron variables, equation (2.22) allows the evaluation of the trace of the product of such two operators in the form:

$$Tr \{AB\rho_{s}\} = Tr \{A\rho_{A}(t')\} Tr \{B\rho_{B}(t')\} .$$  (2.23)

Equation (2.23) has a straightforward physical interpretation: the atomic system and the incident electron are supposed to be uncorrelated at the time the interaction begins, and this uncorrelation is kept up to the time $t$. The approximation described by equation (2.22) is equivalent to the “impact approximation”: the duration of a collision is much smaller than the time between successive collisions. Under this assumption the two systems, namely the atom and the incident electron, can be considered as decoupled. This approximation is reasonable to describe the interaction between atoms and colliding electrons in a large variety of astrophysical plasmas, and more particularly in stellar atmospheres (see, for instance, discussion in Stehle et al. 1983, and references therein quoted).

With respect to the electron beam, we also introduce the further hypothesis that the single electrons are accelerated and directed on the atomic system independently of each other, where by “independently” we mean that there is no definite phase relationship between them. Moreover, any mutual interaction of the electrons during the flight is neglected. In other words, making use of the
terminology of the density matrix theory, we suppose that before the interaction with the atomic system the electronic-beam system is a "statistical mixture" of the individual independent electronic states |ψ⟩. We can formalize the hypothesis above by writing the density operator representing the electron beam in the form
\[
\rho^T = \sum_\psi P_\psi |\psi\rangle\langle\psi|, 
\]
where \(P_\psi\) is the probability of finding a single electron in the pure state |ψ⟩, with the usual normalization condition
\[
\sum_\psi P_\psi = 1. 
\]
As a consequence of the same hypothesis, the electron beam density operator (2.24) has the same expression both in the Shrödinger and in the interaction picture:
\[
\rho^T = \rho^I T. 
\]
As the electronic beam system is an incoherent superposition of the basis states |ψ⟩, its density matrix is diagonal in the \(|\psi\rangle\rangle\) representation:
\[
\langle\psi|\rho^T|\psi\rangle = P_\psi \delta_{\psi\psi}. 
\]
In the following, we will assume that at the beginning of the interaction, the density operator of the electron beam, \(\rho^T(t = 0)\), is of the form given by equation (2.24). This equation allows us to simplify the time evolution equation (2.21). In fact, if we consider operators which do not act on the free electrons variables, it can be shown that the second term appearing in the right-hand side of equation (2.21) is zero. By means of equation (2.23), in fact, this term (for what the part containing the free electrons variables is concerned) can be expressed in the form:
\[
\sum_{l,m} \text{Tr} \left\{ \sum_\psi P_\psi \sum_{\xi} t_{\xi}(l,m) |\xi\rangle\langle\xi| |\psi\rangle\langle\psi| \right\}. 
\]
Because of the orthonormality of the free-electron state vectors (eq. [2.14a]), equation (2.28) simply reduces to
\[
\sum_{l,m} \sum_\psi P_\psi t_{\psi l}(l,m). 
\]
Due to the fact that each electron state vector |ψ⟩ is nothing but a plane wave in the coordinate \(r_p\) times a spin function, we see from the expression of the operator \(T_{\psi l}(r_p)\), given by equation (2.9), that the matrix elements \(t_{\psi l}(l,m)\) factorizes into two parts: an integral over the free electron radial variables times an integral of the form
\[
\int d\Omega Y_{lm}(\vec{\varphi}_p) = (4\pi)^{1/2} \delta_{\lambda\lambda} \delta_{\mu\mu}, 
\]
but as in the interaction Hamiltonian (2.16) there is no \(l = 0\) (monopole) term, equation (2.21) assumes the simpler form:
\[
\frac{d\rho^T}{dt} = \text{Tr} \left\{ \frac{d\tilde{H}(t)}{dt} \rho^T(t) \right\} - \frac{4\pi^2}{\hbar^2} \text{Tr} \left\{ \int_0^\tau \left[ \tilde{H}(t), V(t') \right] \rho^T(t')dt' \right\}, 
\]
which is the basic equation that will be used in the following.
Finally, we will assume a further approximation on the state vectors of the free electrons; namely we will neglect the electronic spin. This will allow us to characterize the free-electron state vectors only by their momentum, so that the state vectors will be from now on denoted by the symbol |\(\psi\rangle\rangle\). In the wave-function representation, we have:
\[
\langle r_p | \psi \rangle = \sqrt{\pi}^{-1/2} \exp \left( \frac{2\pi i}{\hbar} \psi \cdot r_p \right), 
\]
where \(V\) is the volume of the normalization box.

In all the formulae that we have written up to now, the free electron state vectors |\psi⟩ have to be substituted with the symbol |\(\psi\rangle\rangle\); the corresponding energy eigenvalues (in the nonrelativistic approximation) are
\[
E_\psi = \psi^2/2m_e, 
\]
where \(m_e\) is the electron mass.

3. STATISTICAL EQUILIBRIUM EQUATIONS

Taking into account the cyclic property of the trace, the matrix elements \(\rho_{ab}\) of the density operator of the atomic system can be expressed through the projection operators |\(b\rangle\rangle\langle a|\):
\[
\rho_{ab}(t) = \langle a | \rho^T(t) | b \rangle = \text{Tr} \left\{ |b\rangle\langle a| \rho^T(t) \right\}, 
\]
or transforming this expression in the interaction picture:
\[
\rho_{ab}(t) = \text{Tr} \left\{ |b\rangle\langle a| \exp \left( 2\pi i \nu_{ab} t \right) \rho^I(t) \right\}. 
\]
We can express in the same way also the matrix elements \( \rho_{\psi(t)} \) of the density operator which describes the incident electrons at a generic time \( t > 0 \), namely, when the atom-electron interaction has already occurred:

\[
\rho_{\psi(t)} = \langle \psi | \rho_{\psi(t)}^{T} | \psi \rangle = \text{Tr} \{ | \chi \rangle \langle \psi | \exp (2\pi i v_{\psi} t) \rho^{T}(t) \} \, .
\] (3.2b)

[Note that we now use the letter \( \rho \) with greek indices to designate a matrix element of the electron beam operator \( \rho^{T} \), and reserve the latin indices to designate matrix elements of the atomic system operator \( \rho^{A} \).]

The statistical equilibrium equations for the atomic system are obtained considering the time evolution of the quantities \( \rho_{ab} \). Substituting for the operator \( \hat{O}_{i}(t) \) appearing in the time evolution equation (2.31) the projection operator of equation (3.2a), namely

\[
[ b \rangle \langle a | \rho_{ab}(t) \exp (2\pi i v_{ab} t) \cdot
\] (3.3)

we obtain

\[
\frac{d\rho_{ab}(t)}{dt} = -2\pi i v_{ab} \rho_{ab}(t) - \frac{4\pi^{2}}{h^{2}} \text{Tr} \left\{ \int_{0}^{t} \left[ \langle b | \langle a, V_{j}(t') \rangle, V_{i}(t') \rangle \exp (2\pi i v_{ab} t)\rho(t')dt' \right] \right\} .
\] (3.4)

We now evaluate the inner commutator of this equation: remembering expression (2.16) for the interaction Hamiltonian, and taking into account the orthonormality property of the eigenvectors of the atomic Hamiltonian, we have

\[
[|b \rangle \langle a|, V_{f}(t')] = \sum_{l} \sum_{m} \sum_{l'} \sum_{m'} \sum_{a, e, f} \chi_{l, m} \langle t_{z\psi l}(l, m) \exp (2\pi i v_{z\psi l} t) \rangle \\
\times \left[ \sum_{a, e} |c \rangle \langle a, q_{a}(l, m) \exp (2\pi i v_{a}(t) - \sum_{e} |c \rangle \langle a, q_{a}(l, m) \exp (2\pi i v_{a}(t) \rangle \right] .
\] (3.5)

Introducing this result into equation (3.4), we finally get for the double commutator:

\[
[|b \rangle \langle a|, V_{f}(t')] = \sum_{l} \sum_{m} \sum_{l'} \sum_{m'} \sum_{a, e, f} \chi_{l, m} \langle t_{z\psi l}(l, m) \exp (2\pi i v_{z\psi l} t) \rangle \\
\times \left[ \sum_{a, e} |c \rangle \langle a, q_{a}(l, m) \exp (2\pi i v_{a}(t) - \sum_{e} |c \rangle \langle a, q_{a}(l, m) \exp (2\pi i v_{a}(t) \rangle \right] .
\] (3.6)

Inserting this expression into the integral of equation (3.4), and remembering equations (3.2a) and (3.2b), the time evolution equation (3.4) becomes

\[
\frac{d\rho_{ab}(t)}{dt} = -2\pi i v_{ab} \rho_{ab}(t) + \sum_{l} \sum_{m} \sum_{l'} \sum_{m'} \sum_{a, e, f} \chi_{l, m} \langle t_{z\psi l}(l, m) \exp (2\pi i v_{z\psi l} t) \rangle \\
\times \left\{ -q_{a}(l, m)q_{f}(l', m')t_{z\psi l}(l, m)q_{a}(l', m') \int_{0}^{t} \rho_{ab}(t') \rho_{a}(l')(t') \exp (2\pi i v_{a}(t' - t)) dt' \right\} \\
+ q_{a}(l, m)q_{f}(l', m')t_{z\psi l}(l, m)q_{a}(l', m') \int_{0}^{t} \rho_{a}(l') \rho_{a}(l') \exp (2\pi i v_{a}(t' - t)) dt' \\
+ q_{a}(l, m)q_{f}(l', m')t_{z\psi l}(l, m)q_{a}(l', m') \int_{0}^{t} \rho_{a}(l') \rho_{a}(l') \exp (2\pi i v_{a}(t' - t)) dt' \\
- q_{a}(l, m)q_{f}(l', m')t_{z\psi l}(l, m)q_{a}(l', m') \int_{0}^{t} \rho_{a}(l') \rho_{a}(l') \exp (2\pi i v_{a}(t' - t)) dt' .
\] (3.7)

This is the very general equation of motion for determining the evolution of the density matrix elements, \( \rho_{ab}(t) \), of an atomic system interacting with a nonrelativistic electron beam.
Equation (3.7) allows a solution by iteration: if the quantities $\rho_{f0}(t')$, on the right-hand side of equation (3.7) are replaced by their expression obtained from the integration of equation (3.7), the result is a new equation that can be integrated in the same way, so that the new expressions for $\rho_{f0}(t')$ can then be inserted again in equation (3.7), and so on (see, for example, Fujita 1966). The new quantities $\rho_{af}(t')$ could be replaced by a similar series obtained by applying the same iteration technique to the equation for the electron beam analogous to equation (3.7). The successive terms of the series resulting from this iteration procedure correspond to successive Born approximations (see, for instance, Bohm 1951). In the following, we shall retain only the first term, corresponding to a second-order perturbative expansion of equation (3.7). This is simply obtained with the replacements

$$\rho_{ek}(t') \rightarrow \rho_{ek}(0) , \quad (3.8a)$$

and

$$\rho_{f0}(t') \rightarrow \rho_{f0}(0) \quad (3.8b)$$

in the integral of equation (3.7). The use of the above replacements is equivalent to the introduction of the first Born approximation (see, for instance, Moiseiwitsch & Smith 1968). Assumption (3.8a), for instance, means that the incident electron's wave function, that before the collision is represented by a plane wave, is not seriously distorted by the interaction with the target atom so that after the collision it can be still represented to sufficient accuracy by a plane wave. As for the atomic system, assumption (3.8b) means that the perturbation is sufficiently weak so that $\rho_{af}(t')$ are smoothly varying functions, whose characteristic variation time is much longer that the corresponding time over which the exponential in equation (3.7) vary. Therefore, we can consider the quantities $\rho_{f0}$ nearly constant (and in the following it will not be necessary to specify their time argument), so that they may be taken out of the integrals in equation (3.7):

$$\int_0^t dt' \rho_{f0}(t') \rho_{ek}(t') \exp \left[ 2\pi i (v_{be} - v_{ke})(t - t') \right] \approx \rho_{f0} \rho_{ek} \delta_{ek} \int_0^t dt' \exp \left[ 2\pi i (v_{be} - v_{ke})(t - t') \right] , \quad (3.9)$$

where use has been made of expression (2.27) for the density matrix elements of the electron beam. The same assumption of weak atom-electron interaction, which has led to replacements (3.8a) and (3.8b), justifies also the approximation of taking the limit $t \rightarrow \infty$ in order to analytically evaluate the integral in equation (3.9):

$$\lim_{t \rightarrow \infty} \int_0^t \exp \left[ 2\pi i (v_{be} - v_{ke})(t - t') \right] dt' = \frac{1}{2} \int_0^t dt' \exp \left[ \frac{1}{2} v_{be} - v_{ke} \right] = \frac{1}{2} \Phi(v_{be} - v_{ke}) , \quad (3.10)$$

where $\delta(x)$ is the Dirac's delta function and $P$ means the Cauchy's principal part in the distribution theory sense. This limiting procedure is often called the "Van Hove limit" (Van Hove 1955, 1957) or the "long-time approximation" (Kubo, Toda, & Hashitsume 1985). This approximation, together with replacements (3.8a) and (3.8b), is characteristic of what are known in statistical mechanics as the "Markov processes": for all processes in which only the long-time behavior is important, and for which the collisions can be treated as instantaneous, the evolution of a system at a given time $t$ is independent of the knowledge of what the state of the system was before $t$. In Markovian processes, in other words, the system has no "memory", so to say, of its previous history. (See, for instance, Prigogine 1962.)

Taking into account equations (3.9) and (3.10), the time evolution equation (3.7) becomes

$$\frac{d\rho_{ab}}{dt} = -2\pi i v_{ab} \rho_{ab} + \sum_{l=1}^{\infty} \sum_{m=-l}^{l} \sum_{l'=1}^{\infty} \sum_{m'=-l'}^{l'} \frac{2\pi^2}{\hbar^2} \sum_{\xi, \eta, \psi} \sum_{e, b} \left[ \begin{array}{c} -[q_{ab}(l, m) q_{ef}(l', m') \rho_{f0}] [P_{ef} t_{x0}(l, m) t_{x0}(l', m')] \Phi(v_{be} - v_{xe}) \\
+ [q_{ab}(l, m) q_{ef}(l', m') \rho_{f0}] [P_{ef} t_{x0}(l, m) t_{x0}(l', m')] \Phi(v_{be} - v_{xe}) \\
+ [q_{ab}(l, m) q_{ef}(l', m') \rho_{f0}] [P_{ef} t_{x0}(l, m) t_{x0}(l', m')] \Phi(v_{be} + v_{xe}) \\
- [q_{ab}(l, m) q_{ef}(l', m') \rho_{f0}] [P_{ef} t_{x0}(l, m) t_{x0}(l', m')] \Phi^*(v_{be} - v_{xe}) \end{array} \right] , \quad (3.11)$$

where we have suitably redefined the dummy summation indices over the electronic eigenfunctions.

The expression now derived can be conveniently rearranged by observing that, in each of the four terms appearing in the right-hand side, we can distinguish the terms where the atomic energy difference (contained in the delta functions) is nonnegative or nearly zero, the terms where the same difference is negative. For example, the first term can be split into the following ones:

$$\sum_{l=1}^{\infty} \sum_{m=-l}^{l} \sum_{l'=1}^{\infty} \sum_{m'=-l'}^{l'} \left[ \begin{array}{c} -[q_{ab}(l, m) q_{ef}(l', m') \rho_{f0}] [P_{ef} t_{x0}(l, m) t_{x0}(l', m')] \Phi(v_{be} - v_{xe}) \\
+ \sum_{f \geq b} \sum_{e \leq b} \left[ q_{ab}(l, m) q_{ef}(l', m') \rho_{f0} \right] \sum_{f' \geq b} \sum_{e' \leq b} \left[ q_{ab}(l', m') q_{ef}(l, m) \rho_{f0} \right] [P_{ef} t_{x0}(l, m) t_{x0}(l', m')] \Phi^*(v_{be} - v_{xe}) \end{array} \right] , \quad (3.12)$$

where with the symbol $\sum_{a \geq b}$ ($\sum_{a < b}$) we mean that the sum has to be extended to all atomic levels $e$ having energy higher than or equal to (lower than) $b$. To derive this expression we have also made use of the conjugation property

$$\Phi^*(v_{be} - v_{xe}) = \Phi^*(v_{be} - v_{xe}) . \quad (3.13)$$
Dividing up the fourth term in the same way, we have:

\[
\sum_{l=1}^{\infty} \sum_{l'=1}^{\infty} \sum_{m=-l}^{l} \sum_{m'=-l'}^{l'} \left( -\frac{2\pi^2}{\hbar^2} \right) \times \left\{ \sum_{e \neq f} \sum_{q_{ef}^{(l, m)} q_{ef}^{(l', m')}} [P_{\Phi} t_{x\phi}^{(l, m)} t_{\phi x}^{(l', m')} \Phi(v_{\phi x} + v_{x\phi}) + \sum_{e \neq f} \sum_{q_{ef}^{(l, m)} q_{ef}^{(l', m')}} [P_{\phi} t_{x\phi}^{(l, m)} t_{\phi x}^{(l', m')} \Phi(v_{\phi x} + v_{x\phi})] \right\}.
\]

(3.14)

If, in the second term of this expression, we redefine the atomic dummy indices by interchanging \(e\) and \(f\) we obtain

\[
\sum_{l=1}^{\infty} \sum_{l'=1}^{\infty} \sum_{m=-l}^{l} \sum_{m'=-l'}^{l'} \left( -\frac{2\pi^2}{\hbar^2} \right) \times \left\{ \sum_{e \neq f} \sum_{q_{ef}^{(l, m)} q_{ef}^{(l', m')}} [P_{\Phi} t_{x\phi}^{(l, m)} t_{\phi x}^{(l', m')} \Phi(v_{\phi x} - v_{x\phi}) + \sum_{e \neq f} \sum_{q_{ef}^{(l, m)} q_{ef}^{(l', m')}} [P_{\phi} t_{x\phi}^{(l, m)} t_{\phi x}^{(l', m')} \Phi(v_{\phi x} - v_{x\phi})] \right\}.
\]

(3.15)

Taking into account both the Hermitian property of the density operator \((\rho^\dagger = \rho)\) and the conjugate properties of the matrix elements:

\[
[q_{\phi e}^{(l, m)}] = (-1)^m q_{\phi e}^{(l, -m)} ;
\]

\[
[t_{\phi x}^{(l, m)}] = (-1)^m t_{\phi x}^{(l, -m)} ,
\]

(3.16a)

(3.16b)

it is easy to see that if we take the complex conjugate of the first term of expression (3.12) and, at the same time, we interchange its summations' indices \(a\) and \(b\) \((a \neq b)\), we then obtain expression (3.15) (note also that to obtain this identity indices \(m\) and \(m'\) have also to be redefined: \(m \rightarrow -m; m' \rightarrow -m'\)). Analogously, if in expression (3.14) we take the complex conjugate of the first term and we interchange the indices \(e\) and \(f\) having to be interchanged. By performing analogous manipulations on the other terms appearing in equation (3.11), the same can be finally rearranged in the form:

\[
\frac{d\rho_{ab}}{dt} + 2\pi i v_{ab} \rho_{ab} = \sum_{l=1}^{\infty} \sum_{l'=1}^{\infty} \sum_{m=-l}^{l} \sum_{m'=-l'}^{l'} \frac{2\pi^2}{\hbar^2} \times \left\{ -\sum_{f} \sum_{e < b} q_{ef}^{(l, m)} q_{ef}^{(l', m')} [P_{\phi} t_{x\phi}^{(l, m)} t_{\phi x}^{(l', m')} \Phi(v_{\phi x} - v_{x\phi}) + \sum_{e \neq f} \sum_{q_{ef}^{(l, m)} q_{ef}^{(l', m')}} [P_{\phi} t_{x\phi}^{(l, m)} t_{\phi x}^{(l', m')} \Phi(v_{\phi x} - v_{x\phi}) + \sum_{e < b} \sum_{f} q_{ef}^{(l, m)} q_{ef}^{(l', m')} [P_{\phi} t_{x\phi}^{(l, m)} t_{\phi x}^{(l', m')} \Phi(v_{\phi x} + v_{x\phi}) + \sum_{e \neq f} \sum_{q_{ef}^{(l, m)} q_{ef}^{(l', m')}} [P_{\phi} t_{x\phi}^{(l, m)} t_{\phi x}^{(l', m')} \Phi(v_{\phi x} + v_{x\phi}) - \sum_{e \neq f} \sum_{q_{ef}^{(l, m)} q_{ef}^{(l', m')}} [P_{\phi} t_{x\phi}^{(l, m)} t_{\phi x}^{(l', m')} \Phi(v_{\phi x} + v_{x\phi})] + \text{c.c. (}a \neq b\text{) ,}
\right. \]

(3.17)

where the symbol \(\text{"c.c.} (a \neq b)\) \(\) means the quantity which is obtained by taking the complex conjugate of the previous term and interchanging the indices \(a\) and \(b\).

The four lines in the braces represent the contribution to the time evolution of the matrix elements respectively arising from (1) de-excitation of the atomic system toward lower energy levels due to atom-electron superelastic collisions; (2) de-excitation from upper levels due to superelastic collisions; (3) excitation from lower levels due to inelastic collisions; (4) excitation toward upper levels due to inelastic collisions.

It should be noted that the second and the fourth line include the contributions due to the elastic collisions too, provided that \(f = a\). The quantity \(P_{\phi}^{\text{elastic}}\) appearing in equation (3.17) represents the probability of having an incident electron with momentum \(\Psi\) before the collision. On the contrary, \(\chi\) is the free-electron momentum after the collision.

In the next section, we are going to evaluate the sum \(\sum_{\chi}\) over the final momentum eigenstates.

4. INTEGRATION OVER THE FINAL ELECTRONIC STATES

Equation (3.17) involves expressions of the form

\[
\frac{2\pi^2}{\hbar^2} \int_{\chi} t_{\phi x}^{(l, m)} t_{\phi x}^{(l', m')} \Phi(v_{\phi x} - v_{x\phi}) ,
\]

(4.1)

where \(\phi\) and \(x\) are the momenta of the free electron, respectively, before and after the collision with the atom.

\[\text{In order to fully evaluate the whole contribution due to the elastic collisions, also the magnetic terms arising from the relativistic corrections of the interaction}\]

Hamiltonian should be taken into account. In fact, because of the Laporte selection rule, the most conspicuous electrostatic contribution to the elastic collisions is the quadrupole term, which is, however, much less than (or, at most, of the same order of magnitude of) the magnetic dipole term.
Taking the limit \( \nu \to \infty \), we can transform the sum over the electronic eigenvectors in an integral over the momentum phase-space through the expression:

\[
\nu^{-1} \sum_{\chi} \to \frac{\hbar}{2\pi} \int d\Omega_{\chi} \int_0^\infty \chi^{2} d\chi .
\]

(4.2)

On the other hand, the matrix elements \( t_{\nu \chi}(l, m) \) have the following simple form:

\[
t_{\nu \chi}(l, m) = \nu^{-1} \int \exp \left( -\frac{2\pi i}{\hbar} \psi \cdot r_{\rho} \right) T_{\nu \chi}(r_{\rho}) \exp \left( \frac{2\pi i}{\hbar} \chi \cdot r_{\rho} \right) (dr_{\rho})^3
\]

\[
= \nu^{-1} \int \exp (i K u \cdot r_{\rho}) T_{\nu \chi}(r_{\rho}) (dr_{\rho})^3,
\]

(4.3)

where we have introduced the momentum transferred to the atom during the collision through the position:

\[
\chi - \Psi = hKu .
\]

(4.4)

Performing the integration, whose details are given in the Appendix, the following expression can be derived for \( t_{\nu \chi}(l, m) \):

\[
t_{\nu \chi}(l, m) = \left( \frac{4\pi}{2l + 1} \right)^{1/2} \frac{4\pi e^2}{\nu^2} \frac{i^l}{(2l)!!(2l - 1)!!} K^{-2} Y_{\nu \chi}(\partial_{\nu}, \varphi_{\nu}) ,
\]

(4.5)

where \( (\partial_{\nu}, \varphi_{\nu}) \) are the angles relative to the unit vector \( u \), and where \( (2l - 1)!! = 1 \times 3 \times 5 \times \ldots \times (2l - 1) \). In the Appendix, we also show that

\[
t_{\nu \chi}(l, m) = (-1)^m t_{\nu \chi}(l, m).
\]

(4.6)

Referring now to Figure 2, we can express \( K \) through the equation

\[
hK = \left( \psi^2 + x^2 - 2\psi \chi \cos \theta_{\nu} \right)^{1/2} ,
\]

(4.7)

and substituting this result, together with equation (4.5) into equation (4.1), performing transformation (4.2), and taking into account the nonrelativistic energy-momentum relationship (2.35) for a free particle, we finally obtain

\[
\frac{2\pi^2}{\hbar^2} \sum_{\nu} t_{\nu \chi}(l, m) t_{\nu \chi}(l', m') \Phi_{\nu \chi} = \nu^{-1} \frac{16\pi e^2 m_e}{\hbar^2} \frac{i^l}{[(2l + 1)(2l') + 1]^{1/2}(2l - 1)!!(2l' - 1)!!} \times \int d\Omega \chi Y_{\nu \chi}(\partial_{\nu}, \varphi_{\nu}) Y_{\nu \chi}(\partial_{\nu}, \varphi_{\nu}) \int_0^\infty dx x^2 q^{l - r - 3} \Phi (\epsilon_{\nu \chi} + 1 - x^2) ,
\]

(4.8)

where we have introduced the dimensionless quantities \( x, \epsilon_{\nu \chi} \), and \( q \) defined by

\[
x = \frac{\chi}{\psi} ,
\]

(4.9a)

\[
\epsilon_{\nu \chi} = \frac{E_{\nu \chi} - E_e}{\psi^2 / 2m_e} ;
\]

(4.9b)

\[
q = (1 + x^2 - 2x \cos \theta_{\nu})^{1/2} = \frac{hK}{\psi} .
\]

(4.9c)

Note that \( x \) is the momentum of the electron after the collision expressed in terms of its initial momentum; analogously, \( q \) is the momentum lost by the electron in the collision expressed in the same units, while \( \epsilon_{\nu \chi} \) is the energy of the atomic transition expressed in units of the electron initial energy.

We now fix our attention on the integral appearing in equation (4.8). While, on one hand, the integration variables and the quantity \( q \) depend on the angular coordinates of the final momentum \( \chi \); on the other hand, the spherical harmonics are functions of the polar angles of the momentum transfer. Usually, the integration is performed with respect to these last variables (see, for instance, eq. [6.13] in Percival & Seaton 1958). In the present work, however, we will follow an alternative way by integrating over the final momentum variables. This approach, besides being more direct and natural in our formulation, may also turn out to be particularly useful in simplifying the calculation of collisional cross sections corresponding to electric multipole transitions higher than the dipole.

To this aim, the spherical harmonics appearing in equation (4.8) are to be expressed as functions of the angular coordinates of \( \chi \); this can be done through the following formula that has been proved elsewhere (Fineschi & Landi Degl’Innocenti 1990) and is given here in terms of the symbols introduced in equations (4.9) (see also Fig. 2):

\[
P_{\nu \chi}^{(m)}(\cos \theta_{\nu}) = (-1)^{l - |m|} \int_{-1}^{1} \frac{p_{\nu \chi}^{(m)}(\cos (\chi - \theta_{\nu}))}{(1 - \chi)^{l - |m|}} = (-1)^{l - |m|} \sum_{k=0}^{l - |m|} \frac{(-1)^k \Gamma(l + |m|)}{k!} \int_{-1}^{1} (1 - x)^{-k} p_{\nu \chi}^{(m)}(\cos \theta_{\nu}) .
\]

(4.10)
Substituting this result into equation (4.8), and performing the integration with respect to \( \varphi_x \) (which brings a Kronecker delta of the form \( \delta_{-m,m} \)), we obtain

\[
\frac{2\pi^2}{\hbar^2} \sum_{l} \cdots = \psi^{-1} (-1)^m \delta_{-m,m} \frac{8\pi^2 m_e}{\hbar^{l+1'}} \psi^{l+1'-3} \left( \frac{-i}{} \right)^{l+l'} \frac{(2l-1)!!(2l'-1)!!}{(2l+1)!!(2l'-1)!!} \delta_{-m,m} \sum_{k=0}^{-1} \sum_{k'=0}^{-1} \left( \begin{array}{c} l + |m| \\ k \\ \end{array} \right) \left( \begin{array}{c} l' + |m| \\ k' \\ \end{array} \right) \int_{0}^{\infty} dx \Phi(\epsilon_{ae} + 1 - x^2)(-x)^{l'-k-k'+2} \int_{-1}^{1} d\mu \frac{P_{-l}^{|m|}(\mu)P_{-l'}^{|m|}(\mu)}{(1 + \chi^2 - 2x\mu)^2} ,
\]

where in the last integral we have introduced the integration variable \( \mu = \cos \varphi_x \). The imaginary part of the distribution \( \Phi \) (see eq. [3.10]) leads to a diverging integral which is connected to renormalization problems. This part will be simply neglected in our derivation.

We now introduce the following notation:

\[
I_{a,n}^{|m|}(x) = \int_{-1}^{1} d\mu \frac{P_{a}^{|m|}(\mu)P_{n}^{|m|}(\mu)}{(1 + \chi^2 - 2x\mu)^2} .
\]

In order to evaluate the integral with respect to \( x \) in equation (4.12), we observe that, being \( x > 0 \), the Dirac’s delta is satisfied only for

\[
x_0 = (\epsilon_{ae} + 1)^{1/2} .
\]

Obviously, if \( E_a \geq E_e \), that is, if the collision is a superelastic or an elastic one, there is always a value \( x_0 \) such as to satisfy this last equation. Vice versa, if \( E_a \ll E_e \), it may not be possible to satisfy equation (4.14) since the argument of the square root may be negative. This occurs when

\[
\frac{\psi^2}{2m_e} < E_e - E_a
\]

or, in other words, when the energy of the incident electron is less than the threshold energy required to allow the transition. Introducing the quantity

\[
w_{ae}^2 = \epsilon_{ae} + 1 = \frac{E_e - E_a}{\psi^2/2m_e} + 1 ,
\]
and taking into account that, being $x$ positive:

$$\delta(x_0^2 - x^2) = \frac{1}{2|x_0|} \delta(x_0 - x),$$  \hspace{1cm} (4.17)

we obtain for the integral appearing in equation (4.12)

$$\left\{ \begin{array}{ll}
-\frac{i}{2}(-w_{ae})^{r' - k - k' + 1} I_{l, r - k}^{m_l} (w_{ae}), & \text{if } w_{ae}^2 \geq 0; \\
0, & \text{otherwise}.
\end{array} \right.$$  \hspace{1cm} (4.18)

Finally, in order to rewrite equation (4.12) in a more compact form, we introduce the following quantity:

$$\mathcal{G}_l^m(x) = N_l^m \sum_{k=0}^{l-m} \sum_{k'=0}^{l-m} \left( \begin{array}{c}
l + |m| \\
k
\end{array} \right) \left( \begin{array}{c}
l' + |m| \\
k'
\end{array} \right) \delta(x^{r' - k - k' + 1} I_{l-k, r-k}^m (x),$$  \hspace{1cm} (4.19)

where $N_l^m$ is given by

$$N_l^m = \frac{(-1)^l}{2(2l - 1)!!(2l' - 1)!!} \left[ (l - |m|)(l' - |m|)! \right]^{1/2},$$  \hspace{1cm} (4.20)

and satisfies the symmetry property:

$$N_l^m = (-1)^{l'+1} N_{l'}^m.$$  \hspace{1cm} (4.21)

Through these notations, equation (4.12) can be rewritten in the form

$$\frac{2\pi^2}{h^2} \sum_x t_{\varphi l}(l, m) t_{\varphi l}(l', m) \delta(v_{ae} - v_{eg}) = \gamma^{-1}(-1)^m \delta_{-m, m} \frac{8\pi}{a_0^2} k^{l' + r - 4} \mathcal{G}_l^m (w_{ae}),$$  \hspace{1cm} (4.22)

where we have made use of the momentum–wave number relation for a particle:

$$\psi = m_e v_\phi = h k_\phi,$$  \hspace{1cm} (4.23)

and where

$$a_0 = \frac{\hbar^2}{m_e e_0^2}$$  \hspace{1cm} (4.24)

is the Bohr radius.

Equation (4.22) has been derived for a single electron interacting with an atom. This result can be easily generalized to an assembly of uncorrelated electrons by substituting the factor $\gamma^{-1}$ by the electronic density, $N_e$. From now on we will assume such a generalization.

5. THE COLLISIONAL RATES

In this section, we will derive the general expression of the statistical equilibrium equations for an atomic system interacting with a beam of fast electrons.

In § 3, we have evaluated the time evolution of the quantities $\rho_{ab}$, thus obtaining equation (3.17). We now notice that this equation involves general expressions of the form

$$\langle [Q_{ab}(l, m) Q_{cd}(l', m') \delta(v_{ef} - v_{eg})].$$  \hspace{1cm} (5.1)

The bracket can be substituted by the result of the previous section (eq. [4.22]) to obtain

$$\langle [\mathcal{G}_{abdef}] = \sum_{l=1}^{\infty} \sum_{l'=1}^{\infty} \sum_{m=-l}^{l} \sum_{m'=-l}^{l} \sum_{\Psi} P_\Psi N_e v_\phi \frac{8\pi}{a_0^2} k^{l' + r - 4} \sum_m q_{ab}(l, m) q_{cd}(l', m') \mathcal{G}_l^m (w_{ef}),$$  \hspace{1cm} (5.2)

where we have made use of the conjugate property (3.16a). This quantity satisfies the symmetry property

$$[\mathcal{G}_{abdef}]^* = \mathcal{G}_{defab}.$$  \hspace{1cm} (5.3)

The expression now derived for the collisional rate $\mathcal{G}$ involves the evaluation of the matrix elements $q_{ab}$ and $q_{cd}$ that are defined in equation (2.18a). Remembering the definition of the operator $Q_{aal}(r_i)$ given in equation (2.8), we have

$$q_{ab}(l, m) = \frac{4\pi}{2l + 1} \sum_{i=1}^{Z} \langle a_i | r_i^l Y_{lm} (a_i, \varphi_i) | b_i \rangle,$$  \hspace{1cm} (5.4)

where $a_i$ and $a_i$ are the polar angles of the position of the $i$th optical electron with respect to the coordinate system $S$ having its $z$-axis directed along the trajectory of the incident electron.
In many cases, the eigenvectors of the atomic Hamiltonian have to be evaluated in a different reference system, like the system \( S' \) represented in Figure 3. (This may be, for instance, a system whose \( z \)-axis is pointing along the direction of a magnetic field, or along any other physical direction characterizing the medium.) If we denote by \( \theta_i' \) and \( \varphi_i' \) the polar angles of the position of the \( i \)th optical electron in \( S' \), we have

\[
Y_{\ell m}(\theta_i', \varphi_i') = \sum_n Y_{\ell n}(\theta_i', \varphi_i') \mathbb{P}_{nm}(R),
\]

or

\[
Y_{\ell m}(\theta_i, \varphi_i) = \sum_n Y_{\ell n}(\theta_i', \varphi_i') \left[ \mathbb{P}_{nm}(R) \right]^*,
\]

where \( \mathbb{P}_{nm}(R) \) is the rotation matrix, defined according to Brink & Satchler (1968), and \( R \) is the rotation bringing \( S \) into \( S' \): \( R \equiv (-\gamma, -\beta, -\alpha) \) in the notation of Figure 3.

Substituting this last expression in equation (5.4), we obtain the following relation for the matrix elements evaluated in the two reference system:

\[
[q_{\ell n}(l, m)]_S = \sum_n \mathbb{P}_{nm}(R)[q_{\ell n}(l, m)]_{S'},
\]

so that we can write \( \mathcal{E} \) in terms of the matrix elements evaluated in \( S' \):

\[
\mathcal{E}_{abcdef} = \sum_{l=1}^{\infty} \sum_{l'=1}^{\infty} \sum_\varphi P_{\varphi} N_{\varphi} v_{\varphi} \left( \frac{8\pi}{\hbar} \right)^{1/2} \left[ a_{\varphi}' \right]^{l'-4} \sum_{m''} q_{\ell n}(l, m'' \varphi)[q_{\ell n}(l', m'')]^* \sum_{m} \mathbb{P}_{nm}(R)\mathbb{P}_{mn}(R)\mathbb{P}_{m' l'}(w_{el}) .
\]

The statistical equilibrium equation (3.17) can be finally expressed in terms of the quantities \( \mathcal{E} \), like the one given by this last equation, in the more compact form:

\[
\frac{d\rho_{ab}}{dt} + 2\pi i v_{ab} \rho_{ab} = -C_{ab}^{(1)} + C_{ab}^{(2)} + C_{ab}^{(3)} - C_{ab}^{(4)},
\]

where the single collisional rates \( C_{ab}^{(i)}, i = 1, 2, 3, 4 \)—which are graphically represented in Figure 4—are explicitly given by

\[
C_{ab}^{(1)} = \sum_f \sum_{e < b} \mathcal{E}_{ae} \rho_{eb} + \text{c.c.} (a \leftarrow b);
\]

\[
C_{ab}^{(2)} = \sum_e \sum_{f < a} \mathcal{E}_{fb} \rho_{ea} + \text{c.c.} (a \leftarrow b);
\]

\[
C_{ab}^{(3)} = \sum_{e} \sum_{f < a} \mathcal{E}_{be} \rho_{eb} + \text{c.c.} (a \leftarrow b);
\]

\[
C_{ab}^{(4)} = \sum_{e} \sum_{f < a} \mathcal{E}_{ef} \rho_{ea} + \text{c.c.} (a \leftarrow b).
\]
Equation (5.8) is the statistical equilibrium equation for the density-operator matrix elements containing only the collisional rates. Our formalism is however consistent with the one developed in Paper I to deal with an atomic system embedded in a polarized radiation field. If in the frame of the impact approximation introduced in § 2, we make also the further assumption that the collision time is much smaller than the mean time interval between emission or absorption of photons, then the atom-photon and atom-electron interactions can be considered decoupled. Under this assumption the radiative rates derived in Paper I can be directly added to the collisional rates in equation (5.8).

6. THE DIPOLE APPROXIMATION

We now consider the limiting case of the dipole approximation, that is: \( l = l' = 1 \), in order to attain a simplified expression for \( \mathcal{F} \). This will be particularly useful in clarifying the main aspects of the physical phenomena we will describe through our formalism in further papers of this series.

When \( l = 1 \), the operator \( Q_{1,m} \) reduces to

\[
Q_{1,m}(r_i) = \frac{4\pi}{3} \sum_{i=1}^{Z} r_i Y_{1m}^{*}\left(\theta_i, \varphi_i\right).
\]

Introducing the vector

\[
r = \sum_{i=1}^{Z} r_i,
\]

and taking into account the explicit expression for the spherical harmonics, we deduce

\[
Q_{1,0}(r) = r_z;
\]

\[
Q_{1,1}(r) = -\frac{1}{\sqrt{2}} (r_x - ir_y);
\]

\[
Q_{1,-1}(r) = \frac{1}{\sqrt{2}} (r_x + ir_y),
\]

so that, following the Brink & Satchler notations for the spherical components of a vector, we obtain

\[
Q_{1,m}(r) = (-1)^m r_m,
\]

and in turn

\[
q_{ab}(1, n) = (-1)^n \langle a | r_n b \rangle = (-1)^n(r_{-n})_{ab}.
\]

Substituting this result into equation (5.7), we have

\[
\mathcal{E}_{abcdef} = \sum_{\psi} P_{\psi} N_{\psi} \frac{8\pi}{a^2 b^2 c d} \sum_{m=-1}^{1} (-1)^{n+m} (r_{am})(r_{bn})^* \sum_{m'=-1}^{1} \mathcal{E}_{m'm'}(m, m', \Omega_{\psi})\mathcal{E}_{m'm'}^{*}(w_{ef}),
\]

where \( \Omega_{\psi} \equiv \langle \psi | \psi \rangle \) is the direction of the incident electrons having momentum \( \psi \) (before the collision) and where \( \mathcal{E}_{m'm'} \) is the spherical tensor introduced in Paper I:

\[
\mathcal{E}_{m,m'}(m, m', \Omega_{\psi}) = \mathcal{E}_{m,m'}^{(1)}(R)\mathcal{E}_{m,m'}^{(2)}(R).
\]

7. CONCLUSIONS

From the general principles of quantum mechanics we have derived, through the formalism of the density matrix, the statistical equilibrium equations for a multilevel atomic system interacting with an electron beam having an arbitrary angular distribution. The most relevant improvement of the present derivation, with respect to previous ones, is the fact that, besides the coherences among fine and hyperfine structure levels, also the coherences among the Zeeman sublevels split by a magnetic field can be fully accounted for. This result has been achieved by the use of the formalisms: (i) of the tensor operators and (ii) of the density-matrix operator. More specifically:

i. the introduction of spherical tensor operators, whose components transform under a rotation of axes according to a simple law involving the rotation matrices (eqs. [5.5]), allows the derivation of the relevant cross sections in an arbitrary reference frame. Consequently, the expressions for the statistical equilibrium equations we have obtained hold for any arbitrary oriented coordinate system. This result is particularly convenient, for instance, in treating the case of an atomic system collisionally excited in the presence of a magnetic field. In this case, in fact, it is natural to choose as quantization axis the direction of the field because in this reference frame the atomic Hamiltonian is easily diagonalized and the statistical equilibrium equations assume a relatively simpler form;

ii. the formalism of the density-matrix operator allows, through the nondiagonal terms of the atomic density matrix, to account for the coherences among the Zeeman sublevels split by a magnetic field.

In the nonrelativistic limit, and assuming the Born approximation, we have derived analytical expressions for the cross sections of any electric multipole transition concerning elastic, inelastic, and superelastic atom-electron collisions. In general, the cross sections
calculated using the Born approximation are in quite good agreement with experimental measurements, except for energies close to the threshold. This is not, however, a serious limitation for astrophysical applications, where usually the quantities of interest are the rate coefficients, obtained by the convolution of the electron impact cross sections with a given distribution of electron energies. The rate coefficients depend on the number of incident electrons with energy above the threshold, and this number strongly depends on different physical parameters such as, for instance, the temperature. Thus the rates will be much more sensitive to, say, the assumed temperature than to the cross sections, and approximate values can be used pretty safely.

At any rate, more precise cross sections, obtained from theoretical calculations or from experimental measurements, can be always inserted, if necessary, in the collisional rates derived in our theoretical scheme. The replacement of the cross sections obtained in the present work with other cross sections more accurate at threshold is indeed allowed. The reason is that, in our work, the explicit derivation of the collisional rates has been carried out by assuming the Born approximation so that a unified, self-contained formalism could be used. But that approximation has been introduced only when the general expressions for the collisional rates of the statistical equilibrium equations had already been derived (see eq. [3.7]). Thus the final structure of the equilibrium equations and their collisional rates (i.e., eqs. [5.8] and [5.9]) is independent of the Born approximation.

Before applying to astrophysical situations the equilibrium equations derived in the present work, one should first assess the relative importance of the "bath of perturbers" in which the atom is immersed. Indeed, the presence—neglected in our treatment—of other atoms, ions, or thermal electrons with energies below threshold contribute to further perturb the atomic energy levels, leading to a broadening of the absorption and emission spectral lines. In first approximation, the effect of this "bath of perturbers" can be taken into account by replacing the Dirac's delta functions, resulting from our second-order perturbative approach, with "broader" profiles, like, for instance, Lorentzian profiles (see, for example, Griem 1974).

The formalism used to derive the statistical equilibrium equations is fully consistent with the one used in Paper I to derive both the radiative transfer equations for polarized radiation and the equations of the statistical equilibrium for an atomic system embedded in a polarized radiation field. Therefore, the results derived in the present paper and in Paper I can be employed together to write the generalized statistical equilibrium equations for the density matrix of an atomic system interacting both with photons and electrons. These equations are obtained by simply adding the collisional rates to the radiative rates, provided the "impact approximation" be valid, namely, provided the duration of a collision be very short compared to the mean time interval between collisions and with the mean time interval between emission or absorption of photons. The density matrix elements resulting from solving the generalized statistical equilibrium equations can then enter the radiative transfer equations which, once solved, will eventually give the Stokes parameters of the radiation field.

In conclusion, the formalism developed in this paper allows calculations of the polarization in spectral lines of atoms excited by impact of electrons with any anisotropic velocity distribution. The effect of the presence of a magnetic field on this polarization can also be taken into account. Following papers of this series will be devoted to the calculation of impact polarization in different physical regimes of astrophysical interest.

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APPENDIX

In this Appendix we show how the analytical expression (4.5) of the matrix elements \( t_{\varphi_2}(l, m) \) has been derived. We first remember the explicit form of these elements:

\[
\langle \varphi_2 | m \rangle \langle l, m \rangle = \chi^{-1} \int_{\varphi} \exp \left( -\frac{2\pi i}{\hbar} \mathbf{r} \cdot \mathbf{r} \right) T_{lm}(\mathbf{r}) \exp \left( \frac{2\pi i}{\hbar} \mathbf{r} \cdot \mathbf{r} \right) d\mathbf{r} = \chi^{-1} \int_{\varphi} \exp (iK \cdot r) T_{lm}(r) d\mathbf{r},
\]

where \( K = (\chi - \psi)/\hbar \) is the momentum transfer in \( \hbar \) units, and where

\[
T_{lm}(r) = \left( \frac{4\pi}{2l+1} \right)^{1/2} \mathbf{e}_{l+1}^2 \chi_{l}^{(l)}(\theta, \varphi). \]

We develop the exponential through the following multipole expansion:

\[
\exp (iK \cdot \mathbf{r}) = \sum_{n=0}^{\infty} \sum_{q=-n}^{n} \frac{i^n 4\pi j_{n}(Kr)Y_{n}^{(l)}(\theta, \varphi)Y_{n}^{*}(\theta, \varphi)}{r^l} = \sum_{n=0}^{\infty} \sum_{q=-n}^{n} \frac{i^n 4\pi j_{n}(Kr)Y_{n}^{(l)}(\theta, \varphi)Y_{n}^{*}(\theta, \varphi)}{r^l},
\]

where the radial function \( j_{n}(Kr) \) can be expressed through the Bessel functions of half-integer order:

\[
j_{n}(Kr) = \left( \frac{\pi}{2Kr} \right)^{1/2} J_{n+1/2}(Kr),
\]

and where \( (\theta, \varphi) \) are the polar angles of the unit vector \( u \).

Substituting equation (A3) into expression (A1) and taking the limit \( \chi \to \infty \), we obtain

\[
\langle \varphi_2 | m \rangle \langle l, m \rangle = \left( \frac{4\pi}{2l+1} \right)^{1/2} \frac{4\pi e_{l}^{2}}{\chi} \sum_{n=0}^{\infty} \sum_{q=-n}^{n} \int_{\varphi} r^l d\varphi \frac{j_{n}(Kr)}{r^l} Y_{n}^{(l)}(\theta, \varphi) Y_{n}^{*}(\theta, \varphi) Y_{l}(\theta, \varphi),
\]

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which, taking into account the orthonormality property of spherical harmonics, reduces to

\[ t_{\phi_2}(l, m) = \left( \frac{4\pi}{2l+1} \right)^{1/2} \frac{4\pi e_0^2 l^4}{\nu} \left[ \int_0^\infty d\rho \, \frac{j_l(\rho K)}{r_{\rho}^{-1}} \right] Y_{lm}(\vartheta, \varphi) \, . \]  

(A6)

Provided that \( l > 0 \) and \( K > 0 \) [which is always verified in our formulation, since there is no monopole term and, for \( K = 0 \), the diagonal elements \( t_{\phi_2}(l, m) \) vanish], the integral is readily solved (Gradshteyn & Ryzhik 1965; eq. [14], p. 684):

\[ \int_0^\infty d\rho \, \frac{j_l(\rho K)}{r_{\rho}^{-1}} = \frac{K^{l-2}}{(2l-1)!!} \, . \]  

(A7)

Substituting this result into equation (A6), we finally obtain

\[ t_{\phi_2}(l, m) = \left( \frac{4\pi}{2l+1} \right)^{1/2} \frac{4\pi e_0^2 l^4}{\nu} \frac{1}{(2l-1)!!} K^{l-2} Y_{lm}(\vartheta, \varphi) \, . \]  

(A8)

Noting that exchanging \( \chi \) with \( \psi \) is equivalent to substitute \( u \) with \( -u \), we have

\[ t_{\phi_2}(l, m) = \left( \frac{4\pi}{2l+1} \right)^{1/2} \frac{4\pi e_0^2 l^4}{\nu} \frac{1}{(2l-1)!!} K^{l-2} Y_{lm}(\vartheta, \varphi) \, . \]  

(A9)

where \( (\vartheta, \varphi) = (\pi - \vartheta, \pi + \varphi) \) are the polar angles of the direction \( -u \). Because of the well-known parity of the spherical harmonics, we then have

\[ t_{\phi_2}(l, m) = (-1)^l t_{\phi_2}(l, m) \, . \]  

(A10)

REFERENCES

Bohm, D. 1951, Quantum Theory (Englewood Cliffs, NJ: Prentice-Hall)
Moiseiwitsch, B. L., & Smith, S. J. 1968, Rev. Mod. Phys., 40, 238
Oppenheimer, J. R. 1928, Phys. Rev., 32, 361
Percival, I. C., & Seaton, M. J. 1958, Phil. Trans. R. Soc. Lond., A, 251, 113
Van Hove, L. 1955, Physica, 21, 517
— 1957, Physica, 23, 441

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