Collisional-Radiative Models and the Emission of Light

F.B. Rosmej

Sorbonne Universités, Pierre et Marie Curie, Paris, France
and
Ecole Polytechnique, LULI-PAPD, Palaiseau, France
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I. Introduction

Then God said let there be light and there was light.......

*Genesis*
...and since then, light is one of the most fascinating phenomena in nature.....
We all know what light is, but it is not easy to say what it really is...
Historical overview

1180: Nekkam, “magnetic needle”: compass.
1289: Maricourt, reflection of the same type of magnetic poles.
1771, 1773: Cavendish, electrostatic experiments.
1785: Coulomb, electrostatic law of a point charge.
1831: Faraday, electromagnetic induction.
1864: Maxwell, dynamical theory of the electromagnetic field.
1900: Planck, beginning of the quantum theory of light, quantization of the energy of a harmonic oscillator
(ref.: Verhandlungen der Deutschen Physikalischen Gesellschaft 2 (1900), 202 and 237).
1905: Einstein, photoelectric effect, corpuscularity of electromagnetic radiation
(ref.: Annalen der Physik 17 (1905), 132).
1917: Einstein, interaction of electromagnetic radiation with atoms
(ref.: Phys. Z. 18 (1917), 121).
1926: Lewis, the quantum of radiation was named photon
(ref.: G.N. Lewis, Nature 118 (1926), 874).
1963: Glauber, coherent photon states
In 1924 McLennan & Shrum showed in a laboratory experiment (discharge with O + He), that the green color originates from the Oxygen.
Consider a two-level atom:

Line emission $\varepsilon$:

$$\varepsilon = n_1 A_1 h \nu_1 = \frac{\text{energy}}{\text{time} \cdot \text{volume}}$$

$n = \text{atomic population} = \frac{\text{number}}{\text{volume}}$

$A = \frac{\text{number of radiation decays}}{\text{time}}$

$C = \frac{\text{number of collisions}}{\text{time}}$
Collisional-radiative equations

\[ \frac{dn_1}{dt} = n_0 C_{01} - n_1 A_{10} - n_1 \left( C_{10} + C_{d1} \right) \]

Stationary case:

\[ \frac{dn_1}{dt} = 0 \quad \Rightarrow \quad n_1 = \frac{n_0 C_{01}}{A_{10} + C_{10} + C_{d1}} \]

\[ \varepsilon = n_0 C_{01} h \nu_{10} \frac{A_{10}}{A_{10} + C_{10} + C_{d1}} \]
The collisional rate $C$ is proportional to the particle density:

$$C \propto n$$

What happens for low particle densities?

$$A_{10} \gg C_{10} + C_{d1}$$

$$\varepsilon = n_0 C_{01} \hbar \nu_{10} \frac{A_{10}}{A_{10} + C_{10} + C_{d1}} \approx n_0 C_{01} \hbar \nu_{10} \frac{A_{10}}{A_{10}}$$

$$\Rightarrow \quad \varepsilon \approx n_0 C_{01} \hbar \nu_{10}$$

At low particle densities, the intensity $\varepsilon$ turns out to be independent of the transition probability $A$. 

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The water-pool model I.

water population flow

water pool

hole

area A

water loss

$\propto h \cdot A$

excitation rate "C"

atomic population "n"

transition probability "A"

radiation intensity

$\propto n \cdot A$
The water-pool model II.

- Small water population flow
- Excitation rate "C"
- Atomic population "n"
- Transition probability "A"
- Radiation intensity
- Water loss

\[ h=0 \propto C \]

Water flow independent of A

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Why does the red color appear only at large altitudes?
\[ \varepsilon = n_0 C_{01} \hbar \nu^{10} \frac{A_{10}}{A_{10} + C_{10} + C_{d1}} \quad \text{high density} \quad n_0 C_{01} \hbar \nu^{10} \frac{A_{10}}{C_{10} + C_{d1}} \rightarrow 0 \]

all upper level population is quenched by collisions before radiative decay

Quenching condition:
\[ A_{10} \ll C_{10} + C_{d1} \]

\[ A(\text{red}) \approx 10^{-3} \text{ s}^{-1}, A(\text{green}) \approx 10^{-1} \text{ s}^{-1} \]

\[ A(\text{red}) \ll A(\text{green}) \]

The red light is quenched for lower particle densities, so only at high altitudes where the density is low the red light can survive
II. Collisional-Radiative model

Light emission

Atomic population

Theory: collisional-radiative model/atomic kinetics

derive densities, temperatures,.... = diagnostics

non-perturbative
Distribution of ion densities $n_Z$

\[
\frac{d n_Z}{d t} = - n_Z \left( n_e^2 T_{Z,Z-1} + n_e D_{Z,Z-1} + n_e R_{Z,Z-1} + n_e I_{Z,Z+1} \right) \\
+ n_{Z+1} \left( n_e^2 T_{Z+1,Z} + n_e D_{Z+1,Z} + n_e R_{Z+1,Z} \right) \\
+ n_{Z-1} \left( n_e I_{Z-1,Z} \right)
\]

T: 3-body recombination

\[X^{Z+1} + e + e \rightarrow X^Z + e\]

D: dielectronic recombination

\[X^{Z+1} + e \rightarrow X^{Z^{**}}\]
\[X^{Z^{**}} \rightarrow X^Z + \hbar \omega \rightarrow X^Z + \hbar \omega'\]

R: radiative recombination

\[X^{Z+1} + e \rightarrow X^Z\]

I: ionization

\[X^Z + e \rightarrow X^{Z+1} + e + e\]
Charge stage distribution: stationary solution

\[
\frac{n_{Z+1}}{n_Z} = \frac{n_e I_{Z,Z+1}}{n_e R_{Z+1,Z} + n_e D_{Z+1,Z} + n_e^2 T_{Z+1,Z}}
\]

High density limit: \[
\frac{n_{Z+1}}{n_Z} = 2 \left( \frac{m_e k T_e}{2 \pi \hbar^2} \right)^{3/2} \frac{g_{Z+1}}{g_Z} \frac{e^{-E_Z/k T_e}}{n_e} \quad \text{Saha-Boltzmann}
\]

Low density limit: \[
\frac{n_{Z+1}}{n_Z} = \frac{I_{Z,Z+1}}{R_{Z+1,Z} + D_{Z+1,Z}} \quad \text{Corona}
\]

\[
\frac{I_{Z,Z+1}}{R_{Z+1,Z} + D_{Z+1,Z}} = F(T_e) \quad \text{Independent of density!}
\]

\[
n_e^2 T << n_e R + n_e D
\]

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Charge stage distribution of Argon


Spectral distribution

\[ I_{jziz}(\omega) = \frac{\hbar \omega jziz}{4\pi} n_jz A_{jziz} \phi_{jziz}(\omega, \omega jziz) \]

single line transition

\[ I(\omega) = \sum\sum\sum I_{jziz}(\omega) \]

total transitions

Atomic population of level "j" from charge state "Z":

\[ \frac{dn_{jz}}{dt} = -n_{jz} \sum\sum W_{jziz'} + \sum\sum n_{kz'} W_{kz'jz} \]

depopulation population

Population matrix \( W \):

\[ W_{ij} = W_{ij}^{rad} + W_{ij}^{col} \]

\[ W_{ij}^{rad} = A_{ij} + \Gamma_{ij} + P_{ij}^{abs} + P_{ij}^{em} + P_{ij}^{rr} + P_{ij}^{iz} \]

\[ W_{ij}^{col} = n_e C_{ij} + n_e I_{ij} + n_e^2 T_{ij} + n_e R_{ij} + n_e D_{ij} + Cx_{ij} + n_{HP} C_{ij}^{HP} + n_{HP} I_{ij}^{HP} \] ....

Atomic physics processes:

A: radiative decay
\( \Gamma \): autoionization
C: excitation/dexcitation
I: ionization
T: 3-body recombination
R: radiative recombinaton
D: dielectronic recombination

\( P^{abs} \): photoabsorption
\( P^{em} \): stimulated emission
\( P^{rr} \): stimulated rad. recomb.
\( P^{iz} \): photo ionization
\( Cx \): charge exchange
\( C^{HP} \): heavy particle excitation
\( I^{HP} \): heavy particle ionization

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Collisional redistribution between atomic levels is density dependent

Spectral distribution & temperature variations

Resonance line intensity:

\[ I_{k,j'i'}^{\text{res}} = n_e n_k \langle C_{kj'} \rangle \]

Dielectronic satellite line intensity:

\[ I_{k,ji}^{\text{sat}} = n_e n_k \left( \frac{A_{ji}}{\sum_l A_{jl} + \sum_m \Gamma_{jm}} \right) \]

Dielectronic capture rate (\(\Gamma=\)autoionization rate):

\[ \langle D_{kj} \rangle = 1.66 \cdot 10^{-22} \Gamma_{jk} \frac{g_j g_k}{g_k} \exp\left(-\frac{E_{kj}}{kT_e}\right) \left(\frac{kT_e}{c_m^3 s^{-1}}\right)^{3/2} \]

\[ \frac{I_{k,j'i'}^{\text{sat}}}{I_{k',j'i'}^{\text{res}}} = \frac{n_e n(1s) \langle D_{1s-j'} \rangle}{n_e n(1s) \langle C_{1s-j'} \rangle} = \text{function}\left(T_e\right) \]

Line intensity ratios and diagnostics

As atomic populations depend in general on collisional-radiative processes, their population is dependent on density, temperature, hot electrons, ....:

\[
\frac{I_{jziz}}{I_{j'z,i'z}} = \gamma(T_e, n_e, f_{hot}, \ldots)
\]

The ideal case of a temperature diagnostic is identified as:

\[
\frac{I_{jziz}}{I_{j'z,i'z}} = \alpha(T_e)
\]

Dielectronic satellites

The ideal case of a density diagnostic is identified as:

\[
\frac{I_{jziz}}{I_{j'z,i'z}} = \beta(n_e)
\]
Stark broadening of dielectronic satellites

Experiment:
• High-spectral resolution

Theory:
• spectral simulations
• atomic populations/kinetics
• line profiles

Experiment: dense laser produced plasma

Nd-Glass laser: 50 J, 12 ns, Mg-target

\[ \frac{I_{j_1 j_2}}{I_{{j'}_1 {j'}_2}} = \gamma(T_e, n_e, f_{hot}, \ldots) \]

Multiple line ratios are requested

Spectral simulations!

Adds line profile information to line ratios!

Suprathermal electrons are in strong "competition" with bulk electrons.

Hot to distinguish hot electrons from bulk electrons?
Suprathermal electrons II

Qualitative distortion of the distribution of ionic populations:

Charge stages are mixed!

III. Quantum mechanical point of view
Quantum mechanical two-level atom

\[ \hat{H}_E \psi_1 = E_1 \psi_1 \quad \hat{H}_E \psi_2 = E_2 \psi_2 \]

\[ \hbar \omega_0 = E_2 - E_1 \]

\[ \psi_1(\vec{r},t) = e^{-iE_1 t/\hbar} \psi_1(\vec{r}) \]

\[ \psi_2(\vec{r},t) = e^{-iE_2 t/\hbar} \psi_2(\vec{r}) \]

Electromagnetic interaction:

\[ \hat{H} = \hat{H}_E + \hat{H}_{em}(\vec{r},t) \]

\[ \psi(\vec{r},t) = C_1(t) \psi_1(\vec{r},t) + C_2(t) \psi_2(\vec{r},t) \]

\[ C_1(t) H_{11} + C_2(t) e^{-i\omega_0 t} H_{12} = i \frac{\partial C_1(t)}{\partial t} \]

\[ C_1(t) e^{i\omega_0 t} H_{21} + C_2(t) H_{22} = i \frac{\partial C_2(t)}{\partial t} \]

\[ \hbar H_{ij} := \int \psi_i^*(\vec{r}) \hat{H}_1 \psi_j(\vec{r}) dV \]
\( \rho_{11} := |C_1(t)|^2 = \frac{N_1(t)}{N} = \frac{\text{number of ground states}}{\text{total number of atoms}} \)

\( \rho_{22} := |C_2(t)|^2 = \frac{N_2(t)}{N} = \frac{\text{number of excited states}}{\text{total number of atoms}} \)

\( \rho_{12} := C_1(t)C_2^*(t) \quad \rho_{21} := C_1^*(t)C_2(t) \)

**Quantum mechanical populations:**

\[
\frac{d\rho_{22}}{dt} = -\frac{1}{2} iVe^{i(\omega_0-\omega)t}\rho_{12} + \frac{1}{2} iVe^{-i(\omega_0-\omega)t}\rho_{21}
\]

\[
\frac{d\rho_{12}}{dt} = \frac{1}{2} iVe^{-i(\omega_0-\omega)t}(\rho_{11} - \rho_{22})
\]

Diagonal & non-diagonal elements are inherently coupled to each other!

**Heuristic approach:**

\[
\frac{d\rho_{jj}}{dt} = -\rho_{jj} \sum_k W_{jk} + \sum_q \rho_{qq} W_{qj}
\]

Non-diagonal elements do not exist!
Quantum mechanical versus heuristic approach

Straight forward expansion of the density matrix equations in terms of diagonal elements looks not possible.....

Photo-absorption and emission in heuristic approach:

Electromagnetic interaction: \[
\frac{dN_2}{dt} = -N_2A - B\bar{W}N_2 + B\bar{W}N_1
\]

\(A_{21}, B_{12}, B_{21}: Einstein\ coefficients\)

\(\bar{W}: radiation\ field\)

Time dependent solution: \[
N_2(t) = \frac{NB\bar{W}}{A + 2B\bar{W}} \left\{ 1 - e^{-(A+2B\bar{W})t} \right\}
\]

...to be compared with density matrix solution....

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\[
\frac{d\rho_{22}}{dt} = -\frac{1}{2} i V e^{i(\omega_0 - \omega)t} \rho_{12} + \frac{1}{2} i V e^{-i(\omega_0 - \omega)t} \rho_{21} - 2\gamma_{rad}\rho_{22}
\]

\[
\frac{d\rho_{12}}{dt} = \frac{1}{2} i V e^{-i(\omega_0 - \omega)t} \left( \rho_{11} - \rho_{22} \right) - \left( \gamma_{rad} + \gamma_{coll} \right) \rho_{12}
\]

\[
V := \frac{eE_0 X_{12}}{\hbar} \quad \text{Electromagnetic perturbation potential}
\]

\[
X_{12} = \int \psi_1^*(\vec{r}) \cdot \vec{x} \cdot \psi_2(\vec{r}) \, dV \quad \text{Dipole matrix elements}
\]

\[
2\gamma_{rad} = A
\]

\[
\gamma_{coll} = \text{elastic collisions}
\]

No general solution....
.....except for the weak field limit...

\[
\rho_{22}(t) = \frac{1}{4} V^2 \left\{ \zeta_1 + \zeta_2 - 2 e^{- (\gamma_{rad} + \gamma_{coll}) t} \zeta_3 \right\}
\]

\[
\zeta_1 = \frac{(\gamma_{rad} + \gamma_{coll}) / \gamma_{rad}}{(\omega - \omega_0)^2 + (\gamma_{rad} + \gamma_{coll})^2}
\]

\[
\zeta_2 = \frac{\left[ (\gamma_{rad} - \gamma_{coll}) / \gamma_{rad} \right] e^{-2 \gamma_{rad} t}}{(\omega - \omega_0)^2 + (\gamma_{rad} - \gamma_{coll})^2}
\]

\[
\zeta_3 = \frac{\left( (\omega_0 - \omega)^2 + (\gamma_{rad} + \gamma_{coll}) (\gamma_{rad} - \gamma_{coll}) \cos[(\omega_0 - \omega) t] \right)}{(\omega - \omega_0)^2 + (\gamma_{rad} + \gamma_{coll})^2} + \frac{\left[ 2 \gamma_{coll} (\omega_0 - \omega) \sin[(\omega_0 - \omega) t] \right]}{\left( (\omega_0 - \omega)^2 + (\gamma_{rad} + \gamma_{coll})^2 \right) \left( (\omega_0 - \omega)^2 + (\gamma_{rad} - \gamma_{coll})^2 \right)}
\]

Weak field limit in heuristic approach:

\[
N_2(t) = \frac{NB\bar{W}}{A + 2B\bar{W}} \left\{ 1 - e^{- (A + 2B\bar{W}) t} \right\} \quad \text{for } A \gg 2B\bar{W} \quad \Rightarrow \quad N_2(t) = \frac{NB\bar{W}}{A} \left\{ 1 - e^{-At} \right\}
\]
.....except for the weak field limit...

\[
\rho_{22}(t) = \frac{1}{4} V^2 \left\{ \xi_1 + \xi_2 - 2 e^{-(\gamma_{\text{rad}} + \gamma_{\text{coll}}) t} \xi_3 \right\}
\]

\[
\xi_1 = \frac{(\gamma_{\text{rad}} + \gamma_{\text{coll}})/\gamma_{\text{rad}}}{(\omega - \omega_0)^2 + (\gamma_{\text{rad}} + \gamma_{\text{coll}})^2}
\]

\[
\xi_2 = \frac{\left[ (\gamma_{\text{rad}} - \gamma_{\text{coll}})/\gamma_{\text{rad}} \right] e^{-2\gamma_{\text{rad}} t}}{(\omega - \omega_0)^2 + (\gamma_{\text{rad}} - \gamma_{\text{coll}})^2}
\]

\[
\xi_3 = \frac{\left[ (\omega_0 - \omega)^2 + (\gamma_{\text{rad}} + \gamma_{\text{coll}})(\gamma_{\text{rad}} - \gamma_{\text{coll}}) \cos[(\omega_0 - \omega)t] \right]}{\left[ (\omega_0 - \omega)^2 + (\gamma_{\text{rad}} + \gamma_{\text{coll}})^2 \right] \left[ (\omega_0 - \omega)^2 + (\gamma_{\text{rad}} - \gamma_{\text{coll}})^2 \right]} + \frac{2\gamma_{\text{coll}} (\omega_0 - \omega) \sin[(\omega_0 - \omega)t]}{\left[ (\omega_0 - \omega)^2 + (\gamma_{\text{rad}} + \gamma_{\text{coll}})^2 \right] \left[ (\omega_0 - \omega)^2 + (\gamma_{\text{rad}} - \gamma_{\text{coll}})^2 \right]}
\]

Weak field limit in heuristic approach:

\[
N_2(t) = \frac{NB\bar{W}}{A + 2B\bar{W}} \left\{ 1 - e^{-(A+2B\bar{W}) t} \right\} \quad \text{A} \gg 2B\bar{W} \rightarrow N_2(t) = \frac{NB\bar{W}}{A} \left\{ 1 - e^{-At} \right\}
\]

Both equations have still nothing in common...
I. "Broad band illumination":

Frequency spread of the radiation field exceeds considerably the line width \(2(\gamma_{\text{rad}} + \gamma_{\text{coll}})\):

\[
\int_{-\infty}^{+\infty} \rho_{22} \, d\omega = \frac{\pi V^2}{4\gamma_{\text{rad}}} \left\{ 1 - e^{-2\gamma_{\text{rad}} t} \right\}
\]

II. Large collisional broadening: \(\gamma_{\text{coll}} \gg \gamma_{\text{rad}}\)

\[
\rho_{22} = \frac{(\gamma_{\text{rad}} + \gamma_{\text{coll}}) V^2 / 4\gamma_{\text{rad}}}{(\omega_0 - \omega)^2 + (\gamma_{\text{rad}} + \gamma_{\text{coll}})^2} \left\{ 1 - e^{-2\gamma_{\text{rad}} t} \right\}
\]

(provides also line profile)
I. "Broad band illumination":

frequency spread of the radiation field exceeds considerably the line width $2(\gamma_{\text{rad}} + \gamma_{\text{coll}})$:

$$\int_{-\infty}^{+\infty} \rho_{22} \, d\omega = \frac{\pi V^2}{4\gamma_{\text{rad}}} \left\{ 1 - e^{-2\gamma_{\text{rad}}t} \right\}$$

II. Large collisional broadening: $\gamma_{\text{coll}} \gg \gamma_{\text{rad}}$

$$\rho_{22} = \frac{(\gamma_{\text{rad}} + \gamma_{\text{coll}}) V^2 / 4\gamma_{\text{rad}}}{(\omega_0 - \omega)^2 + (\gamma_{\text{rad}} + \gamma_{\text{coll}})^2} \left\{ 1 - e^{-2\gamma_{\text{rad}}t} \right\}$$

Looks similar to

$$N_2(t) = \frac{NB\overline{W}}{A} \left\{ 1 - e^{-At} \right\}$$

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IV. Conclusion and outlook

- Most of light emission is atomic in origin and therefore subject to quantum effects
- Atomic populations determine the spectral distribution of the light emission
- Collisional-radiative processes determine the atomic populations
- Simulation of the atomic populations allow to draw conclusions: temperature, density, hot electrons,....

- Quantum mechanical description: density matrix
- The relation between quantum and heuristic approach is not simple.... and has not yet been solved for realistic multi-level systems
- Einstein theory invalid for high intensities: the Einstein coefficients are not constant, 1st order perturbation theory, rotating wave approximation, random orientation,...