Influence of electron-impact excitation on the radiation line profile in an electric field

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The influence of collisional excitation mechanisms on spectral line shape is studied theoretically. The influence of an external electric field on line shape formation has been investigated using the density matrix representation. The He atom transition lines $4^1P_1 - 2^1S_0$, $4^1P_1 - 2^1P_1$, $4^1D_2 - 2^1S_0$, $4^1D_2 - 2^1P_1$, $4^1F_3 - 2^1S_0$, $4^1F_3 - 2^1P_1$ are considered.

Introduction

Spectral line shape is an important object of study in spectroscopy. This is connected with its role in the study of mechanisms of elementary processes in plasma, as well as with problems of plasma diagnostics.

It should be noted that line shape is a very sensitive instrument in plasma diagnostics. The availability of information on this object allows one to determine the distribution functions of perturbing particles, particularly those with pronounced anisotropic properties.[1–5] Besides, diagnostics based on spectral line shape are indispensable for studying spectra with overlapping contours.

Although spectral broadening theory is quite well developed,[6] it deals, as a rule, with isotropic mechanisms of broadening. On the other hand, it is well known that anisotropic mechanisms of spectral line broadening may significantly alter the line shape and cause it to be asymmetrical.

The works of Rebane[7–9] were the first to investigate the influence of anisotropic collisions on line shape. Later,[10–13] the theory of anisotropic broadening of spectral lines of atoms and ions colliding with beams of charged and neutral particles was elaborated using the density matrix apparatus.

In addition to anisotropic collisional mechanisms, characteristics of plasma emission are strongly affected by the presence of an external electric field. In particular, we have shown[14–15] that an electric field induces changes in the polarization and angular radiation characteristics comparable to the effects of anisotropic collisions.

In this work we theoretically investigate the influence of collisional excitation mechanisms on spectral line shape in an external electric field for the case of atomic excitation by electron impact.

1. Atomic emission line shape in an external electric field

The spectral line shape is the Fourier transform of the correlation function $F(t)$ describing the time dependence of state of the atom[16]

$$I(\omega) = \frac{1}{\pi}\,\mathrm{Re}\int_0^\infty F(t)\,\mathrm{e}^{-i\omega t}\,\mathrm{d}t\,. \tag{1}$$

In the density matrix representation the correlation function is described by the elements of the density matrix $\rho_{M_0M_0}$ of the atomic state $|M_0>$ after photon emission, which is related to the density matrix $\rho_{MM'}$ of the atomic states $|M>$ before emission through the radiation transition operator $\mathbf{D}$

$$F(t) = \sum_{M_0} \rho_{M_0M_0} = \sum_{\substack{M_0\\ MM'}} < M_0|(\mathbf{eD})|M > < M'|(\mathbf{eD})^+|M_0 > \rho_{MM'}. \tag{2}$$

The density matrix $\rho_{MM'}$ of an atom is determined by the elementary processes in which the atom has participated prior to emission. Thus, the line shape carries information about all the processes taking place in the plasma.

In the presence of an external electric field, it is necessary to describe the atomic state in terms of the Stark wave functions $|M>$ and $|M_0>$ which in the expansion of an isolated atom in terms of the wave functions $|J'M>$ have the form

$$|M> = \sum_{J'} C_{J'}|J'M>. \tag{3}$$

Let the atom after a photon emission pass into the state $|M_0>$ which is not perturbed by the field: $|M_0> = |J_0M_0>$.

Introducing the polarization tensor $t_q^{(k)}$ by expanding in terms of the spherical components of the polarization vector $\mathbf{e}_\lambda$

$$t_q^{(k)} = \sum_{q_1q_2} (-1)^q \sqrt{2k+1} \begin{pmatrix} 1 & 1 & k \\ q_1 & -q_2 & -q \end{pmatrix} e^{(1)}_{q_1} e^{(1)}_{q_2}, \tag{4}$$

we arrive at the following expression for the line shape in the dipole approximation:

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$$I(\omega) = \frac{1}{\pi} \sum_{M_0 M} \sum_{J'J''} \sum_{\substack{k\,q \\ q_1 q_2}} (-1)^{q_1} \sqrt{2k+1} \times$$
$$\times \begin{pmatrix} J_0 & J' & 1 \\ M_0 & -M & -q_1 \end{pmatrix} \begin{pmatrix} J_0 & J'' & 1 \\ M_0 & -M & -q_2 \end{pmatrix} \begin{pmatrix} 1 & 1 & k \\ q_1 & -q_2 & -q \end{pmatrix} \times$$
$$\times\, t^{(k)}_{q}$$
$$\mathrm{Re}\left\{ < J_0 \parallel D^{(1)} \parallel J' > < J_0 \parallel D^{(1)} \parallel J'' >^* \times \right.$$
$$\left. \times\, C_{J'}(M)\, C^*_{J''}(M) \int_0^\infty \rho_{MM}(t)\, \mathrm{e}^{-i\omega t}\, \mathrm{d}t \right\}, \qquad (5)$$

where $\rho_{MM}(t)$ is a solution of the kinetic equation for the density matrix,[17] which takes into account the processes in which the atom has participated.

As can be seen from Eq. (5), the line shape for the transition $J \to J_0$ is a superposition of contours created separately by each state $|M>$.

2. Kinetic equations for elements of the density matrix $\rho_{MM}(t)$ in an external electric field

The kinetic equation for the elements of the density matrix $\rho_{MM}(t)$ which take into account collisional excitation of an atom and spontaneous emission in an external electric field has the form

$$\dot{\rho}_{MM} = -(\Gamma_{MM} - i\omega_M)\,\rho_{MM} + \left(\sum_{M_0} N^{MM}_{M_0 M_0}\, \rho_{M_0 M_0} \right) f_N(t), \qquad (6)$$

where Γ_{MM} is the inverse lifetime of the atom's Mth level, $N^{MM}_{M_0 M_0}$ is the excitation matrix describing the Mth state of the atom excited by electron impact. The function $f_N(t)$ describes the time dependence of the excitation.

In the case of uniform population of the lower state $\rho_{M_0 M_0}$, the general solution of the kinetic equation takes the form

$$\rho_{MM} = \left(\sum_{M_0} N^{MM}_{M_0 M_0}\ \rho_{M_0 M_0}(0) \right) \mathrm{e}^{-(\Gamma_{MM} - i\omega_M)t} \times$$
$$\times \int_0^t f_N(t')\, \mathrm{e}^{(\Gamma_{MM} - i\omega_M)t'}\, \mathrm{d}t' \,. \qquad (7)$$

It follows from Eqs. (5)–(7) that in the case of quasistationary excitation the M-component of the line shape includes the Lorentz and dispersion contours, as well as the Fourier transform of the excitation function

$$\mathrm{Re} \int_0^\infty \rho_{MM}(t)\, \mathrm{e}^{-i\omega t}\, \mathrm{d}t =$$
$$= \rho_{M_0 M_0}(0) \left(\sum_{M_0} N^{MM}_{M_0 M_0} \right) \frac{\Gamma^2_{MM}}{(\Gamma^2_{MM} + \omega^2_M)} \frac{1}{(\Gamma^2_{MM} + (\omega - \omega_M)^2)} -$$
$$- \rho_{M_0 M_0}(0) \left(\sum_{M_0} N^{MM}_{M_0 M_0} \right) \frac{\omega_M}{(\Gamma^2_{MM} + \omega^2_M)} \frac{(\omega - \omega_M)}{(\Gamma^2_{MM} + (\omega - \omega_M)^2)} +$$
$$+ \rho_{M_0 M_0}(0) \left(\sum_{M_0} N^{MM}_{M_0 M_0} \right) \frac{\Gamma_{MM}}{(\Gamma^2_{MM} + \omega^2_M)}\, \mathrm{Re} \int_0^\infty f_N(t)\, \mathrm{e}^{-i\omega t}\, \mathrm{d}t. \qquad (8)$$

Numerical calculations show that the ratios of the amplitudes of the dispersion line shape to the Lorentz line shape and of the Fourier transform of the excitation function to the dispersion line shape in the case of spontaneous emission are less than unity. Therefore, the Lorentz line shape plays the main role in the formation of the line shape's M-component. The presence of a constant dispersion component leads to asymmetry even of those emission lines, in the formation of which only one M-component participates. The relative contribution of the Fourier transform of the excitation function is so negligible that it cannot noticeably affect the spectral line shape.

In the formation of line shapes with short inverse lifetimes ($\Gamma_{MM} \ll \Delta\omega_D$) the Doppler effect must be taken into account. Then, after averaging Eq. (8) over velocities via the distribution function of the emitting atoms, the line shape's M-component will be a superposition of the Doppler line shape $\frac{1}{\sqrt{\pi}\Delta\omega_D} \times \exp\left[-\left(\frac{\omega - \omega_M}{\Delta\omega_D} \right)^2 \right]$ and the corresponding dispersion line shape $\frac{(\omega - \omega_M)}{\sqrt{\pi}\Delta\omega_D} \exp\left[-\left(\frac{\omega - \omega_M}{\Delta\omega_D} \right)^2 \right]$.

3. Excitation matrix in the case of He atom excitation by electron impact in an external electric field

In the case of He atom excitation by electron impact, in the electron velocity distribution function $f_e(\mathbf{v})$ a slow (Maxwell) and a fast (beam) part may be distinguished:

$$f_e(\mathbf{v}) = W\left\{ \exp\left[-(\mathbf{v} - \mathbf{v}_d)^2 / v_0^2 \right] + \gamma\delta(\mathbf{v} - \mathbf{v}_b) \right\}.$$

Here $\mathbf{v}_d$ is the drift velocity of the slow electrons, $\mathbf{v}_b$ is the velocity of the beam electrons, v_0 is the velocity of thermal motion of the electron, W is a normalization factor, and γ is the contribution of the beam electrons.

To form the excitation matrix $N^{MM}_{M_0 M_0}$ in terms of the density matrix representation in an external electric field, we write the slow part in the form of an expansion over multipole moments $f^{(k)}_0(v)$ (Ref. 14)

$$f_e(\mathbf{v}) = W\left[\sum_k f^{(k)}_0(v) Y^{(k)}_0(\Omega) + \gamma\delta(\mathbf{v} - \mathbf{v}_b) \right]. \qquad (9)$$

The multipole moments $f_0^{(k)}(v)$ of the distribution function can be found from the inverse transform

$$f_0^{(k)}(v) = \int \exp\left[-(\mathbf{v} - \mathbf{v}_d)^2/v_0^2\right] Y_0^{(k)*}(\Omega)\,d(\Omega). \quad (10)$$

Expanding the exponential in a series up to the fourth order inclusive, we obtain the following expressions for the multipole moments $f_0^{(k)}(v)$ of rank k = 0, 1, and 2:

$$f_0^{(0)}(v) = 2\sqrt{\pi}\, e^{p_1^2} e^{p_2^2 v^2} \left(1 + \frac{2}{3} p_1^2 p_2^2 v^2 + \frac{2}{15} p_1^4 p_2^4 v^4\right),$$

$$f_0^{(1)}(v) = 4\sqrt{\frac{\pi}{3}}\, e^{p_1^2} e^{p_2^2 v^2} p_1 p_2 \left(v + \frac{2}{5} p_1^2 p_2^2 v^3\right),$$

$$f_0^{(2)}(v) = \frac{8}{3}\sqrt{\frac{\pi}{5}}\, e^{p_1^2} e^{p_2^2 v^2} p_1^2 p_2^2 \left(v^2 + 2 p_1^2 p_2^2 v^4\right), \quad (11)$$

where $p_1 = v_d/v_0$, $p_2 = v_1/v_0$, v_1 is the velocity corresponding to the excitation threshold, and v is the relative velocity of the slow electrons measured in units of v_1.

Using the well-known dependence of the atomic excitation cross section on the relative energy of the exciting electrons u (Ref. 16)

$$\sigma(J', J_0) = N_a [\pi a_0^2]\, v \left(\frac{Ry}{\Delta E(J', J_0)}\right)^2 \left(\frac{E(J')}{E(J_0)}\right)^{3/2} \times$$
$$\times \frac{Q^{(x)}(J', J_0)}{(2l_0 + 1)} G(J') \sqrt{\frac{u}{u+1}} \frac{u}{u + \varphi(J')},$$

we arrive at the following expression for the excitation matrix:

$$N_{M_0' M_0''}^{M' M''} = \frac{4\sqrt{2\pi}\, N_a [\pi a_0^2]}{\sqrt{m_e}} \frac{Ry^2}{(kT)^{3/2}} \sum_{J'J''} C_{J'}^*(M')\, C_{J''}(M'') \times$$
$$\times \sqrt{G(J')\, G(J'')} \left(\frac{E(J')\, E(J'')}{E(J_0)\, E(J_0)}\right)^{3/4} (2L_0 + 1) \times$$
$$\times \sqrt{(2J' + 1)(2J'' + 1)(2L' + 1)(2L'' + 1)} \times$$
$$\times \sum_{\substack{M_1' M_1'' \\ M_{00}' M_{00}''}} (-1)^{J' + J'' + M_0' - M'' - M_1'' - M_{00}''} \times$$
$$\times \sum_{\substack{xk \\ k_1 k_2}} (2k_1 + 1)(2k_2 + 1)\sqrt{2k + 1} \begin{pmatrix} J_0 & J' & k_1 \\ M_0' & -M' & -q_1 \end{pmatrix} \times$$
$$\times \begin{pmatrix} J_0 & J'' & k_2 \\ M_0'' & -M'' & -q_1 \end{pmatrix} \begin{pmatrix} J_0 & J' & x \\ M_{00}' & -M_1' & q \end{pmatrix} \begin{pmatrix} J_0 & J' & k_1 \\ M_{00}' & -M_1' & q \end{pmatrix} \times$$
$$\times \begin{pmatrix} J_0 & J'' & x \\ M_{00}'' & -M_1'' & q \end{pmatrix} \begin{pmatrix} J_0 & J'' & k_2 \\ M_{00}'' & -M_1'' & q \end{pmatrix} \times$$
$$\times \begin{pmatrix} k_1 & k_2 & k \\ q & -q & 0 \end{pmatrix} \begin{pmatrix} k_1 & k_2 & k \\ q_1 & -q_1 & 0 \end{pmatrix} \begin{Bmatrix} L_0 & J_0 & S \\ J' & L' & x \end{Bmatrix} \times$$
$$\times \begin{Bmatrix} L_0 & J_0 & S \\ J'' & L'' & x \end{Bmatrix} \begin{Bmatrix} l_0 & L_0 & L_p \\ L' & l' & x \end{Bmatrix} \begin{Bmatrix} l_0 & L_0 & L_p \\ L'' & l'' & x \end{Bmatrix} F_0^{(k)}(J', J''),$$

where

$$F_0^{(k)}(J', J'') =$$
$$= \int_0^\infty f_0^{(k)}(v) \sqrt{\frac{v^2 - 1}{(v^2 + \varphi(J') - 1)(v^2 + \varphi(J'') - 1)}}\, v^2\, dv.$$

Numerical calculations of the He-atom excitation states 4^1P_1, 4^1D_2, and 4^1F_3 show that the relative populations of the magnetic sublevels of the atomic excited states vary as the external electric field strength is increased. Therefore, as can be seen from Eq. (8), an external electric field alters the amplitudes of the line shape's M-components.

4. Calculational results

Line shapes were computed for the He-atom transitions $4^1P_1 - 2^1S_0$, $4^1P_1 - 2^1P_1$, $4^1D_2 - 2^1S_0$, $4^1D_2 - 2^1P_1$, $4^1F_3 - 2^1S_0$, and $4^1F_3 - 2^1P_1$ for field strengths from 0 to 90 kW/cm at a gas pressure of 1–10 Torr and gas temperature of 300 K.

The computations show that an external electric field contribute significantly to the formation of the excitation line shape of a He atom excited by electron impact. An electric field induces a splitting of the magnetic sublevels and, correspondingly, a shift of the line shape's M-components. The spacing between the M-components can reach 1 nm. Redistribution of the magnetic sublevel population of the excited atom in an electric field results in the predominant population of one M-component, which, according to Eq. (8), alters the amplitude of the M-component of the corresponding line shape. In addition, the line shape's M-component acquires a dispersion component. Its contribution, in contrast to collisional relaxation,[9] reaches 20–30%.

Conclusion

Our calculations show that an external electric field exerts a significant effect on collisional and emission processes in a plasma. This effect manifests itself in an additional redistribution of the populations and shifts of the Stark levels excited by an electron beam.

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