Calculation of the Emission Spectra of Atoms and Ions in the External Electric Field

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Abstract - In the present work a method for calculation of emission spectra of atoms and ions in an alternating circular polarized electric field is proposed. The method allows one to investigate the energy structure of spectra, transition probabilities, and spectral line intensities depending on frequency and strength of the electric field. As an illustration, the emission spectrum of a helium atom is calculated at the electric field strength up to 1kV/cm.

1. Introduction

An electric field is always present in plasma either as the external field maintaining a discharge or the internal one inside of a plasma micro-field formed by charged particles of plasma. The presence of this field leads not only to the Stark effect as such, but also to the fact that other atomic characteristics such as transition probabilities, lifetimes, and spectral line intensities show a dependence on changes in the parameters of the electric field.

The most of experimental and theoretical methods of investigation into the influence of the electric field on emission of atoms and ions concern with the study of this influence on the energy structure of spectra alone. As to transition probabilities, lifetimes, and spectral line intensities of emission spectra, theoretical methods for calculation of these characteristics are elaborated mainly for the static or quasi-static electric fields. The calculation methods for the static electric field are well developed for hydrogen-like and helium atoms (see [1,2] and references therein) in the electric field, however, these methods are not suitable for other atoms. A comprehensive study of transition probabilities and spectral line intensities was performed for rare gas atoms in the static electric field [3]. It should be noted that modern computers allow calculation of transition probabilities, it is though complicated but solvable problem. However, in calculating spectral line intensities essential difficulties arise. This is connected with the necessity of calculation of level populations, electron temperatures, and so on. In the case of LTE-plasma or under condition of the Boltzman excitation source, the calculation of the level populations is relatively not complicated, hence the calculation of spectral line intensities is greatly simplified [4].

In the case of the alternating electric field, theoretical methods of calculation of the Stark effect are well developed (see [5-7] and references therein). However, the calculation methods for transition probabilities are elaborated much worse than for the case of the static electric field, and they can be applied only under great limitations and simplifications. A general method for calculation of spontaneous transition probabilities for atoms and ions in the external circular polarized electric field was suggested in [8].

Some problems arise in calculation of the intensity of emission spectrum of atoms and ions in the alternating electric field. This is due to the fact that the transition probabilities and lifetimes depend on the frequency and strength of the electric field, and level populations are determined by the mechanism of discharge excitation. Thus, the calculation of spectral line intensities represents a set of problems, and each problem needs an adequate choice of a theoretical model and time-consuming computation. Nowadays few calculations of spectral line intensities in plasma were performed, for example, in [9]. However, in view of the complexity of this problem, systematic calculations of intensities of emission spectra for atoms and ions in plasma, especially in nonequilibrium plasma, are absent.

In the present work, a method for calculation of the intensity of emission spectra for atoms and ions in the alternating circular polarized electric field is suggested. The electric fields of such polarization are observed both in high-frequency discharges [10] and under laser excitation [11]. The proposed method allows to us to investigate the dependence of transition probabilities and spectral line intensities on frequency and strength of the electric field.

2. Calculation method

In a circular polarized electric field, a non-stationary Schrödinger equation is written as

$$i\frac{\partial \psi_n(\vec{r},t)}{\partial t} = (\hat{H}_0(\vec{r}) - eF(x\cos\omega t \pm y\sin\omega t))\psi_n(\vec{r},t), \quad (1)$$

where ψ_n is the wave function of the n-th state of a system, $\hat{H}_0(\vec{r})$ is the unperturbed Hamiltonian, and the operator $-eF(x\cos\omega t \pm y\sin\omega t)$ describes perturbation induced by the interaction of an atom with a circular polarized field of frequency ω and strength F. The «+» and «–» signs correspond to the right and left

polarization of the field, respectively. To go to a stationary Schrödinger equation, let us use the rotating-wave approximation [12].

In order to go to a rotating coordinate system rotating around the *Z*-axis with the frequency ω, let us introduce a wave function in this coordinate system

$$\varphi(\vec{r},t) = \exp(i\omega t\hat{J}_z)\psi(\vec{r},t) \ , \qquad (2)$$

where $\hat{J}_z$ is the z-component of the total angular momentum operator. After substitution of the wave function (2) in Eq. (1), we get

$$i\frac{\partial\varphi(\vec{r},t)}{\partial t} = \hat{Q}\varphi(\vec{r},t), \quad \hat{Q} = (\hat{H}_0 - \omega\hat{J}_z \pm F\hat{D}_x) \ . \qquad (3)$$

As seen from Eq. (3), the operator $\hat{Q}$ is time-independent. Hence, in the rotating-wave approximation, it is possible to go from the non-stationary Schrödinger equation (1) to the stationary one, and we get

$$\hat{Q}\varphi(\vec{r}) = \varepsilon\varphi(\vec{r}) \qquad (4)$$

whence

$$\varphi(\vec{r},t) = \exp(-i\varepsilon t)\varphi(\vec{r}) \qquad (5)$$

The operator $\hat{Q}$ is the operator of the energy of an atom in an electric field, and ε and $\varphi(\vec{r},t)$ are the energy and wave function of the atom in the electric field in the rotating coordinate system.

It was shown in [7] that the wave functions and energies of the atom, being the solutions to the Schrödinger equation (4), can be found from the diagonalization of the $\hat{Q}$ matrix. This matrix is obtained in the representation of the unperturbed wave functions $\varphi_n^{(0)}$ calculated in the absence of external electric field. In this representation, the matrix elements of the energy operator $\hat{Q}$ are written as

$$\begin{aligned} Q_{mn} &= E_n^{(0)}\delta_{mn} - \\ &\omega < \varphi_m^{(0)}(\vec{r})\left|\hat{J}_z\right|\varphi_n^{(0)}(\vec{r}) > \pm F < \varphi_m^{(0)}\left|D_x\right|\varphi_n^{(0)} > \end{aligned}, \qquad (6)$$

where $E_n^{(0)}$ is the energy of the *n*-th state of an atom in the absence of external electric field, *F* and ω are the strength and frequency of the external electric field and D_x is the x-component of the dipole transition operator.

The diagonalization of the energy matrix with elements (6) gives a set of wave functions and the energy spectrum for the n-states of the atom in the electric field. Upon diagonalization of the $\hat{Q}$ matrix, we get the energies ε_n and wave functions as

$$\varphi_n(\vec{r},t) = e^{-i\varepsilon_n t}\sum_k C_{nk}\varphi_k^{(0)}(r) \qquad (7)$$

for the n states of the atom in the external electric field in the rotating coordinate system. The coefficients C_{nk} in the wave function (7) depend on the frequency and strength of the external electric field. To find the average energies of the atom in the initial coordinate system, it is necessary to perform averaging over the oscillation period. Upon averaging, the average energy of the system in the electric field in the initial coordinate system is written in the following form

$$\begin{aligned} \overline{E}_n &= < \psi_n(\vec{r},t)\left|H(\vec{r},t)\right|\psi_n(\vec{r},t) > = \\ &\varepsilon_n + \omega < \varphi_n(\vec{r})\left|\hat{J}_z\right|\varphi_n(\vec{r}) > \end{aligned} \ . \qquad (8)$$

It follows from Eq. (8) that $\overline{E}_n$ is time-independent.

The matrix elements of the D_x operator are calculated as follows:

$$\begin{aligned} &< \varphi_m^{(0)}\left|D_x\right|\varphi_n^{(0)} > = < \gamma JM\left|D_x\right|\gamma' J'M' > = \frac{(-1)^{J-M}}{\sqrt{2}} \\ &\left[\begin{pmatrix} J & 1 & J' \\ -M & -1 & M' \end{pmatrix} - \begin{pmatrix} J & 1 & J' \\ -M & 1 & M' \end{pmatrix}\right] < \gamma J\left\|D\right\|\gamma' J' > \end{aligned} \qquad (9)$$

the reduced matrix elements $< \gamma J\left\|D\right\|\gamma' J' >$ are calculated depending on a coupling scheme. Details of calculation of these matrix elements are represented in [8,13].

The wave functions and energies derived from the diagonalization of the $\hat{Q}$ matrix are used for the calculation of the probabilities of spontaneous atomic transitions in the electric field. In the dipole approximation, the probability of spontaneous radiation of a photon to an element of the space angle dΩ from the |n> state to the |m> state with the polarization $\boldsymbol{e_q}$ is determined by the formula

$$A_q = \frac{\omega^3}{hc^3}\left|\mathbf{e_q} < \Psi_n \mid \mathbf{D} \mid \Psi_m >\right|^2 d\Omega \, , \qquad (10)$$

where ω is the transition frequency, $\mathbf{D} = -e\sum_i \mathbf{r_i}$ is the dipole momentum of an atom, and Ψ_n and Ψ_m are the wave functions of the *n*-th and *m*-th states of the atom in the external electric field. Based on Eq. (10), the total transition probability for a radiation polarized with respect to the $\boldsymbol{e_q}$ direction and averaged over all possible orientations in space of the vector $\boldsymbol{D}$ is calculated using the formula

$$A_{nm} = \frac{4\omega^3}{3\hbar c^3}\sum_q \left| < \Psi_n \mid D_q \mid \Psi_m > \right|^2 , \qquad (11)$$

where D_q are the cyclic components of the vector $\boldsymbol{D}$. The wave functions Ψ_n are determined from the diagonalization of the $\hat{Q}$ matrix with the matrix elements (6). On substituting the wave functions Ψ_n and Ψ_m to Eq. (11) and using the Wigner–Eckart theorem, the expression for the probability of the $JM \rightarrow J'M'$ transition between magnetic energy sublevels becomes

$$A(JM \rightarrow J'M') = \frac{4\omega_{JM,J'M'}^3}{3\hbar c^3} \mid D_{JM,J'M'} \mid^2 ,$$

$$D_{JM,J'M'} = \sum_q \sum_{ij} C_i^{(JM)*} C_j^{(J'M')} (-1)^{J_i - M_i} \cdot$$

$$\begin{pmatrix} J_i & 1 & J_j \\ -M_i & q & M_j \end{pmatrix} \cdot < \gamma_i J_i \| D \| \gamma_j J_j >, \quad (12)$$

where $C_i^{(JM)}$ and $C_j^{(J'M')}$ are the expansion coefficients of the wave functions for an atom in the electric field in terms of the unperturbed wave functions $\varphi_i^{(0)}(\gamma_i J_i M_i)$ and $\omega_{JM,J'M'}$ is the frequency of the $JM \to J'M'$ transition. The probabilities for the $J \to J'$ transitions between energy levels are calculated using formula

$$A(J \to J') = \frac{1}{2J+1} \sum_{MM'} A(JM \to J'M'). \quad (13)$$

An absolute intensity of the Stark level in the emission spectrum is determined by expression

$$I(JM \to J'M') = N_{JM} A(JM \to J'M') \hbar \omega_{JM,J'M'}, \quad (14)$$

where N_{JM} is the population of magnetic sublevel and A(JM→ J′M′) is the transition probability from Eq. (12). So, for calculation of spectral line intensities for an atom in the electric field it is necessary to know the populations of magnetic sublevels. For plasma in thermodynamic equilibrium, the level populations are estimated from the Boltzman distribution. In the case of nonequilibrium emission spectra for estimation of the character of level populations of atoms in the electric field, one can use the static and dynamic approximations proposed in [2,14]. In the static approximation, it is assumed that the same number of atoms is situated at each magnetic sublevel on the average over time, and we have

$$N_J = N_{JM}(2J+1). \quad (15)$$

In the dynamic approximation, it is assumed that the same number of atoms get to each Stark sublevel per unit of time, in this case, the population N_J is proportional to the lifetime of state [14]

$$N_J = N_0 \tau(JM). \quad (16)$$

The dynamic approximation gives good agreement with the experimental data at pressure up to 10^{-4}Torr, while the static approximation allows us to obtain satisfactory results from the pressure 10^{-2}Torr. In a high-frequency discharge where small pressure ~2Torr is observed, the assumption on uniform population of magnetic sublevels (15) is quite justified. The populations of the Stark levels can be obtained from the population density balance equations. A computer code for solving these equations was written within of the given INTAS project by N. Denisova [15].

3. Results and discussion

As an illustration, the method considered in section 2 was applied to the calculation of the dynamic Stark effect, transition probabilities and intensity of emission spectrum for a He atom. This atom was exposed to the circular polarized electric field of frequency ω=100MHz and strength up to 1kV/cm. The calculations were carried out with the *LS*-coupling scheme, and *ns-, np-, nd-* and *nf*-states with the main quantum number *n* up to 10 were taken into account. In calculating the energy matrix of the He atom in the electric field 115 energy levels (501 magnetic sublevels) were included. The dependence of the shift and splitting of spectral lines of the foregoing atom on the strength of the electric field is shown in Fig.1.

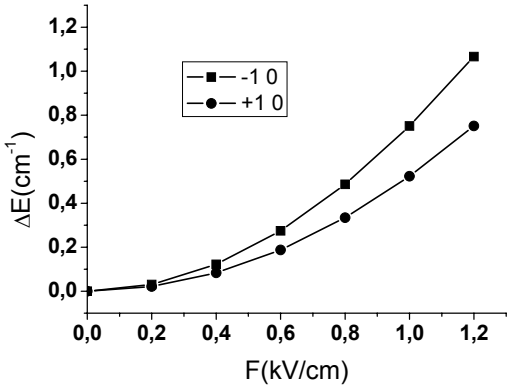

Fig.1. Dependence of the Stark effect on the electric field strength for the 8^1P_1–2^1S_0 spectral line, λ=329.772nm

The distribution of transition probabilities for the np^1P_1-$2s^1S_0$ and nd^3D_1-$2p^3P_0$ spectral lines for the He atom is plotted in Fig.2. In this figure the quantity

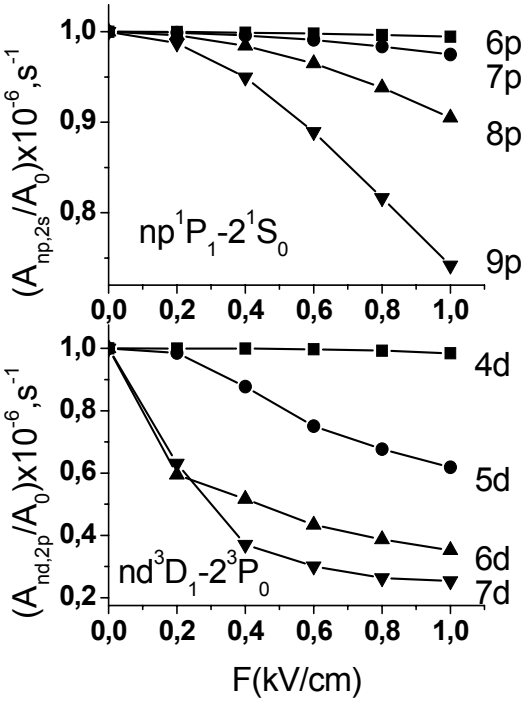

Fig.2. Dependence of the transition probabilities on the electric field strength

$A_{JJ'}/A_0$ is the relation of the transition probabilities $A_{JJ'}$ to the probability A_0, where A_0 is the transition probability of the considered transition in the absence of the electric field. Fig. 2 shows that all transition probabilities decrease with an increase in the strength of the electric field.

Further, Fig. 3 shows that there is some anisotropy of the transition probabilities for the He atom.

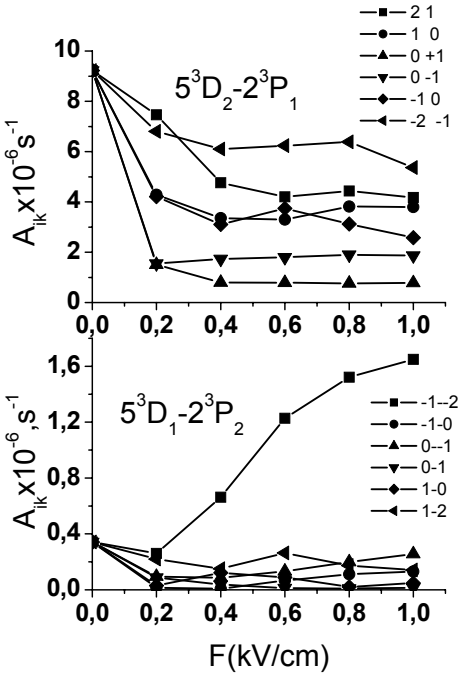

Fig.3. Anisotropy of the transition probabilities for the He atom

It follows from an analysis of the wave functions that this anisotropy is induced by an interaction between magnetic sublevels because the electric field mixes energy levels. Fig. 4 shows behaviour of the spectral line intensities depending on the electric field strength.

As seen from this figure, intensities of the considered spectral lines decrease with an increase in the electric field strength.

4. Conclusions

Suggested in the present work method allows us to calculate spectra of atoms and ions in the circular polarized electric field with frequency lying in the range from radio- up to optical frequencies and at electric field strength changing into wide range. Obtained from these calculations regularities can be used both for the purposes of modeling of processes taking place in plasma and for plasma diagnostics.

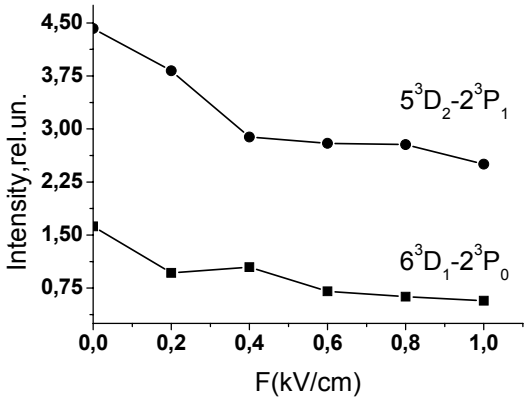

Fig.4. Dependence of the spectral line intensities on the electric field strength

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