Abstract – In this paper, a special software package is suggested to simulate the emission spectra of atoms and ions in an alternating electric field of a circular polarization. The electric field of such polarization can be produced by a high-frequency discharge and under laser excitation. In the framework of a theoretical approach realized in the suggested package, it is possible to calculate the dynamic Stark effect, transition probabilities, and lifetimes of atoms and ions in the electric field. In order to demonstrate the package facilities, emission spectra of rare gases in the electric field were calculated, because these gases are widely used in plasma physics. Using this software package, the dependences of shifts and splitting of spectral lines, transition probabilities and lifetimes on the electric-field strength and frequency were investigated for the He, Ne, Ar, and Kr atoms. Several interesting regularities were revealed based on the simulation results. The simulation procedure can be useful for plasma diagnostics and interpretation of experimental data.

1. Introduction

An electric field is always present in plasma either as an external field maintaining the discharge or an internal one inside the plasma micro-field formed by charged particles. 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, and lifetimes show a certain dependence on changes in the parameters of the electric field. Of special interest is the investigation of the Stark effect and other characteristics of rare-gas atoms in the electric field since these gases are widely used for plasma processing.

The spectra of atoms subjected to an alternating electric field are determined from the non-stationary Schrödinger equation. The methods of solution of this equation depend on the type of field polarization (linear, circular or elliptic polarization). In this paper, we consider the dynamic Stark effect for the case of a circular polarized field. Electric fields of such polarization may be observed in a high-frequency discharge in electrodeless lamps [1] and under laser excitation [2]. In a circular polarized electric field, the solution of the Schrödinger equation is significantly simplified because of separation of spatial and time variables. Due to this separation, the non-stationary Schrödinger equation is reduced to the stationary one within the rotating-wave approximation [3].

In the present work, a theoretical method suggested in [4] was applied to solution of the stationary Schrödinger equation. The wave functions and energies determined by this method were further used for calculation of the transition probabilities and lifetimes of atoms in the electric field. These results are topical in plasma physics, because the data are necessary for understating of the processes occuring in plasma.

2. Calculation method

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

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

where \( \psi_n \) is the wave function of the \( n \)-th state of the 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 \( \omega \) and strength \( F \). To go to the stationary Schrödinger equation, let us use the rotating-wave approximation [3].

In order to go to a rotating coordinate system rotating around the Z-axis with the frequency \( \omega \), let us introduce a wave function in this coordinate system

$$\phi(\vec{r}, t) = \exp(i \omega t \hat{J}_z) \psi(\vec{r}, t),$$  \hspace{1cm} (2)

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

$$\frac{i}{\hbar} \frac{\partial \phi(\vec{r}, t)}{\partial t} = \hat{Q} \phi(\vec{r}, t), \hspace{1cm} \hat{Q} = (\hat{H}_0 - \omega \hat{J}_z \pm F \hat{D}_z). \hspace{1cm} (3)$$

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

$$\hat{Q} \phi(\vec{r}) = \exp(\hat{Q}),$$  \hspace{1cm} (4)

where

$$\phi(\vec{r}, t) = \exp(-i \omega t) \phi(\vec{r}),$$  \hspace{1cm} (5)
Where \( n \) is the state number of the atom and the field, and \( E_n \) is the energy of the system in the electric field, in the rotating coordinate system. The coefficients \( C_{ij} \) in the matrix \( Q \) are calculated as follows:

\[
Q_{nm} = E_n^{(0)} \delta_{nm} - \omega < \varphi_n(r) | \mathbf{J} | \varphi_n(r) > + F < \varphi_n^{(0)} | D | \varphi_n^{(0)} > ,
\]

where \( \varphi_n^{(0)} \) and \( E_n^{(0)} \) are the wave function and energy of the \( n \)-th state of an atom in the absence of external electric field, \( F \) and \( \omega \) are the strength and frequency of the external electric field, and \( D \) is the component of the dipole transition operator.

Diagonalization of the energy matrix with elements (6) gives a set of wave functions and an energy spectrum for the \( n \)-states of the atom in the coordinate system. Upon diagonalization of the \( Q \) matrix, we get the energies \( E_n \) and wave functions as

\[
\varphi_n(r, t) = e^{-\mathbf{Q}t} \sum_i C_{ik} \varphi_i^{(0)}(r)
\]

for the \( n \) states of the atom in the external electric field in the rotating coordinate system. The coefficients \( C_{ik} \) in wave function (7) depend on the frequency and strength of the 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:

\[
\bar{E}_n = < \psi_n(r, t) | H(r, t) | \psi_n(r, t) > = E_n + \omega < \varphi_n(r) | \mathbf{J} | \varphi_n(r) > .
\]

It follows from Eq. (8) that \( E_n \) is time-independent.

The matrix elements of the \( D \) operator are calculated as follows:

\[
< \varphi_n^{(0)} | D | \varphi_n^{(0)} > = < \gamma J M | D | J' M' > = \frac{(\mathbf{J} \cdot \mathbf{M}) (-1)^{J-M}}{\sqrt{2}} = \left[ \begin{array}{cc} J & J' \\ -M & -M' \end{array} \right] \left[ \begin{array}{cc} J & J' \\ -M & -M' \end{array} \right]^\dagger < \gamma J | D | \gamma J' > ,
\]

the reduced matrix elements \( < \gamma J | D | \gamma J' > \) are calculated depending on a coupling scheme. Details of calculation in [5].

The wave functions and energies derived from diagonalization of the \( Q \) matrix are used for the calculation of the probabilities of spontaneous atomic and ionic transitions in the electric field. In the dipole approximation, the probability of spontaneous radiation of a photon to an element of the space angle \( d\Omega \) from the \( |m> \) state to the \(|m'> \) state with the polarization \( \mathbf{e}_q \) is determined by the formula

\[
A_q = \frac{\omega^3}{\hbar c^3} | < \Psi_n | D | \Psi_m > |^2 d\Omega ,
\]

where \( \omega \) is the transition frequency, \( D = -e \sum_i r_i \) is the dipole moment of an atom, and \( \Psi_n \) and \( \Psi_m \) 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 of a radiation polarized with respect to the \( \mathbf{e}_q \) direction and averaged over all possible orientations in the vector \( D \) space is calculated using the formula

\[
A_{nm} = \frac{4\omega^3}{3\hbar c^3} \sum_q < \Psi_n | D_q | \Psi_m >^2 ,
\]

where \( D_q \) are the cyclic components of vector \( D \). The wave functions \( \Psi_n \) are determined from the diagonalization of the \( Q \) matrix with the matrix elements (6). On substituting the wave functions \( \Psi_n \) and \( \Psi_m \) to Eq. (11) and using the Wigner–Eckart theorem, the expression for the probability of the \( J_1 \rightarrow J_2 \) transition between magnetic energy sublevels becomes [5]

\[
\frac{A_{J_1J_2}}{A_{J_1'J_2'}} = \sum_q C_{J_1J_2}^{q,q'} C_{J_1J_2}^{q,q'} < \gamma J | D | \gamma J > ,
\]

where \( C_{J_1J_2}^{q,q'} \) and \( C_{J_1J_2}^{q,q'} \) are the expansion coefficients from Eq. (7) and \( \phi_{J_1J_2} \) is the frequency of the \( J_1 \rightarrow J_2 \) transition. The probabilities of the \( J \rightarrow J' \) transitions between energy levels are calculated using the formula

\[
A(J \rightarrow J') = \frac{1}{2J+1} \sum_{m=\pm J} A(J \rightarrow J') .
\]

Finally, the \( J \)-state lifetime \( \tau_J \) of an atom or ion in the electric field is calculated using the following formula

\[
\tau_J = \sum_J \frac{1}{A(J \rightarrow J')} .
\]

As seen from the above formulas, our theoretical method is free from limitations inherent in the pertur-
bation theory and allows us to simulate emission spectra of atoms and ions in a wide range of electric-field strengths and frequencies.

The algorithm of using this method was realized in a special software package written in FORTRAN. A block diagram of this package is shown in Fig. 1.

![Block diagram of the software package for simulation of emission spectra](image)

3. Results and discussion

In the present work, an electric field of strength up to 10 kV/cm and different frequencies, namely, \( \omega = 100 \text{ MHz} \), \( \omega = 241.813 \cdot 10^5 \text{ MHz} \), and \( \omega = 283.005 \cdot 10^6 \text{ MHz} \) was considered. The electric fields of such frequencies are produced by real excitation sources, \( \omega = 100 \text{ MHz} \) is the electric-field frequency in a high-frequency discharge in electrodeless lamps [1], \( \omega = 241.813 \cdot 10^5 \text{ MHz} \) is the frequency of CO\(_2\) laser and \( \omega = 283.005 \cdot 10^6 \text{ MHz} \) is the frequency of Nd-laser. Only spectral lines in the visible spectral region were examined, but other spectral regions also can be studied with no limitations. The calculations were performed with the LS coupling scheme for the He atom, and the JL coupling scheme for the rest rare-gas atoms. In calculations of the He, Ne and Ar spectra the ns-, np-, nd- and nf-states with the main quantum number \( n \) up to 10 were taken into account, whereas for the Kr atom, the same states were taken into account, but with \( n \) up to 13.

The simulation has allowed us to find a number of regularities in the emission spectra of rare-gas atoms in the electric field. Firstly, the direction of the spectral-line shift is changed to the opposite one for the spectral lines as the nuclear charge of the rare-gas atom is increased. As an illustration, Fig. 2 shows the behaviour of the spectral lines of the Ne, Ar, and Kr atom in the electric field.

![The Stark effect for spectral lines of rare-gas atoms](image)

For all spectral lines of rare-gas atoms, the dependence of the spectral line shift is quadratic with respect to the electric-field strength. And, as a rule, the higher the energy level from which the transition occurs, the greater the shift and splitting of the corresponding spectral line. All exceptions from these rules are connected with strong interaction between energy levels in the electric field. It is obvious, the energy-level interactions increase with the electric-field strength, which causes an increase in the energy-level shifts and splitting. Further, our calculations have shown that an increase in the frequency of the electric field leads to a decrease in the shift and splitting of the Stark levels. As an illustration, Fig. 3 shows the shift and splitting of the \( 9f \) spectral line for the Kr atom in the electric fields of different frequency. One of possible reasons for the decrease in shifts and splitting of spectral lines with growth of the electric field frequency is a decrease in the interaction between the energy levels.
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Fig. 3. The dynamic Stark effect versus electric-field frequency for the $^9P_3 - ^9P_2$ spectral line of the Kr atom

Secondly, forbidden spectral lines induced by the energy-level interactions appear due to the electric field. The probabilities of appearance of these lines increase with the electric-field strength (see Fig. 4).

Fig. 4. Allowable and forbidden transition probabilities versus electric-field strength for the He atom ($\omega = 100 \text{ MHz}$)

As seen from this figure, the forbidden transition probabilities increase fast and become comparable with the allowed ones as the electric-field strength is increased.

Thirdly, the calculation results have demonstrated that, as a rule, the transition probabilities decrease with an increase in the electric-field strength, but sometimes this regularity is broken. Moreover, some anisotropy of the transition probabilities can be observed (see Fig. 5).

Fig. 5. Transition probabilities for the $^5D_2 - ^2P_0$ spectral line versus electric-field strength ($\omega = 100 \text{ MHz}$)

4. Conclusion

It is well known, that simulation is a powerful instrument for a comprehension of physical reality. The obtained results are useful for understanding the processes taking place in plasma and for plasma diagnostics, in particular, for determination of the electric-field strength inside a discharge. Calculation of the transition probabilities between energy levels can clarify the mechanism of filling of the excited-state energy levels for atoms and ions in the external electric field. Moreover, based on these calculations, an increase/decrease in intensities of spectral lines and their broadening in the electric field can be predicted.

References