On the Influence of the Electronic Structure of Atoms on the Behavior of Radiation Transition Probabilities in Alternating Electric Fields

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Abstract— In this work, it is shown that the behavior of transition probabilities in emission spectra of rare gases, induced by alternating circular electric field, is specified by the electronic structure of atomic states. The method of the energy matrix diagonalization for an atom in the electric field free from limitations of perturbation theory was used for our theoretical calculations. In the framework of this method, regularities in the behavior of transition probabilities in emission spectra of rare gas atoms were revealed. The found regularities have allowed us to classify the behavior of considered probabilities according to the electronic structure of the Stark states participating in the transition.

1. INTRODUCTION

A theoretical study of emission spectra of atoms in alternating electric fields is a topical problem of modern physics with a lot of practical applications. The behavior of spectra is characterized by the positions of the Stark components of spectral lines and transition probabilities between the Stark states. To calculate these spectral characteristics, a reliable and efficient method is required.

To calculate emission spectra of atoms excited by optical lasers, a theoretical method based on non-stationary perturbation theory was developed [1]. However, other excitation sources (electrodeless high-frequency lamps, light-emitting diodes, terahertz lasers, and so on) have appeared by the present time. These sources generate electric fields with parameters essentially different from electric field parameters of optical lasers. Non-stationary perturbation theory, by virtue of its limitations, is unsuitable for calculating emission spectra excited by such sources. This fact necessitates the creation of a new theoretical approach for calculating atomic emission spectra in alternating electric fields. Such approach was suggested and developed in [2, 3] for the case of a circularly polarized electric field. This method is free from limitations of perturbation theory and valid in a wide range of changes in the frequency and strength of the electric field.

In this work, regularities in the behavior of transition probabilities between the Stark states of atoms at changes in the frequency and strength of a circular electric field were investigated within the suggested method. Rare gas He, Ne, Ar, and Kr atoms were chosen as subjects for study, because these atoms are widely used in different excitation sources. The calculations have shown that the behavior of transition probabilities in emission spectra of considered atoms is specified by the electronic structure of atomic Stark states participating in the transition.

2. THEORETICAL METHOD

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

$$i\frac{\partial\psi_n(\vec{r},t)}{\partial t} = \left(\widehat{H}_0(\vec{r}) - F\left(x\cos\omega t \pm y\sin\omega t\right)\right)\psi_n(\vec{r},t), \tag{1}$$

where ψ_n is the wave function of the n-th state of the system, $\widehat{H}_0(\vec{r})$ is the unperturbed Hamiltonian, and the operator $-F(x\cos\omega t \pm y\sin\omega t)$ describes perturbation induced by the interaction of an atom with a circularly 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 the stationary Schrödinger equation, it is necessary to use the rotating-wave approximation [4]. In the framework of this approximation, the wave function in the coordinate system rotating around the Z-axis with the frequency ω, has the form

$$\varphi(\vec{r},t) = \exp\left(i\omega t\widehat{J}_z\right)\psi(\vec{r},t), \tag{2}$$

where $\widehat{J}_z$ is the z-component of the total angular momentum operator. On substituting Eq. (2) in Eq. (1), we get

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

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

$$\widehat{Q}\varphi(\vec{r}) = \varepsilon\varphi(\vec{r}), \quad \varphi(\vec{r},t) = \exp(-i\varepsilon t)\varphi(\vec{r}) \tag{4}$$

where $\widehat{Q}$ is the operator of energy of an atom in the electric field, and ε and $\varphi(\vec{r},t)$ are the energy and wave function of an atom/ion in the electric field in the rotating coordinate system. Instead of solving the Schrödinger equation within perturbation theory, it is much more convenient to solve this equation by the method of the energy matrix diagonalization [2, 3]. It was shown in [3] that the wave functions and energies of the atom and ion, being solutions to the Schrödinger Eq. (4), are determined from diagonalization of the energy matrix with elements

$$Q_{mn} = E_n^{(0)}\delta_{mn} - \omega\left\langle\varphi_m^{(0)}(\vec{r})\left|\widehat{J}_z\right|\varphi_n^{(0)}(\vec{r})\right\rangle \pm F\left\langle\varphi_m^{(0)}\left|D_x\right|\varphi_n^{(0)}\right\rangle, \tag{5}$$

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, and D_x is the x-component of the dipole transition operator. Diagonalization of the energy matrix with elements (5) gives a set of wave functions and an energy spectrum for the n-states of the atom in the electric field. Upon diagonalization of the energy matrix, we get the energies ε_n and wave functions as

$$\varphi_n(\vec{r},t) = e^{-i\varepsilon_n t}\sum_k C_{nk}\varphi_k^{(0)}(r) \tag{6}$$

for the n states of the atom/ion in the electric field in the rotating coordinate system. The coefficients C_{nk} in the wave functions (6) depend on the electric field frequency and strength. After averaging over the oscillation period, the average energy of the atom in the electric field in the initial coordinate system is written as

$$\bar{E}_n = \left\langle\psi_n(\vec{r},t)\left|H(\vec{r},t)\right|\psi_n(\vec{r},t)\right\rangle = \varepsilon_n + \omega\left\langle\varphi_n(\vec{r})\left|\widehat{J}_z\right|\varphi_n(\vec{r})\right\rangle. \tag{7}$$

It follows from Eq. (7) that $\bar{E}_n$ is time-independent. The matrix elements of the D_x operator in Eq. (5) are calculated as follows

$$\begin{aligned}\left\langle\varphi_m^{(0)}\left|D_x\right|\varphi_n^{(0)}\right\rangle &= \left\langle\gamma JM\left|D_x\right|\gamma' J'M'\right\rangle \\ &= \frac{(-1)^{J-M}}{\sqrt{2}}\left[\begin{pmatrix} J & 1 & J' \\ -M & -1 & M'\end{pmatrix} - \begin{pmatrix} J & 1 & J' \\ -M & 1 & M'\end{pmatrix}\right]\left\langle\gamma J\left\|D\right\|\gamma' J'\right\rangle\end{aligned} \tag{8}$$

where the reduced matrix elements $\langle\gamma J\|D\|\gamma' J'\rangle$ are calculated depending on a coupling scheme within the formalism of irreducible tensor operators. Details of calculating these matrix elements are reported in [3, 5].

As seen from the above reasoning, the proposed approach is free from limitations of perturbation theory, and it may be applied to calculations of spectral characteristics of any atom in a circularly polarized electric field of an arbitrary strength and frequency. The developed theoretical approach was implemented in a special software package StarkD written in FORTRAN.

3. RESULTS AND DISCUSSION

In the framework of the suggested approach, the calculations were performed within the *LS*-coupling scheme for the He atom, and within the *Jl*-coupling scheme for the rest rare gas atoms. A simulation of the behavior of transition probabilities in electric fields of different strengths and frequencies has allowed us to classify the behavior of these probabilities versus the transition type and the degree of energy state mixtures in the electric field. The type of the $JM \rightarrow J'M'$ transition is specified by the quantum numbers J and J', and the degree of the Stark state mixtures is determined by the quantum numbers n and l of the electron from the external electron shell. An analysis of wave functions has shown that a weak interaction of the Stark states is typical for low-lying atomic states (at small n). The degree of interaction of these states increases with n. As for the dependence of the degree of state mixtures on the quantum number l of the electron from the shell from which

the transition occurs, ns states practically do not mix even for the large principal quantum number n, and the Stark state interactions increase with l.

Based on the electronic structure of atomic states and the degree of the Stark state interactions, the following classification of the types of behavior for transition probabilities $A(JM \to J'M')$ with changes in the electric field F and electric field frequency ω has been established.

1) For weak mixture of the Stark states, all $M \to M'$ transitions are equiprobable (at $J, J' \leq 1$) and pairwise equiprobable (at $J, J' \geq 2$), and the transition probabilities decrease with increasing electric field strength (see Table 1). For strong interactions of states, all $M \to M'$ transitions are unequiprobable, and transition probabilities can either decrease or increase with increasing F (Figs. 1 and 2). The larger the quantum numbers n and l, the greater is the difference between probabilities of the $M \to M'$ transitions.

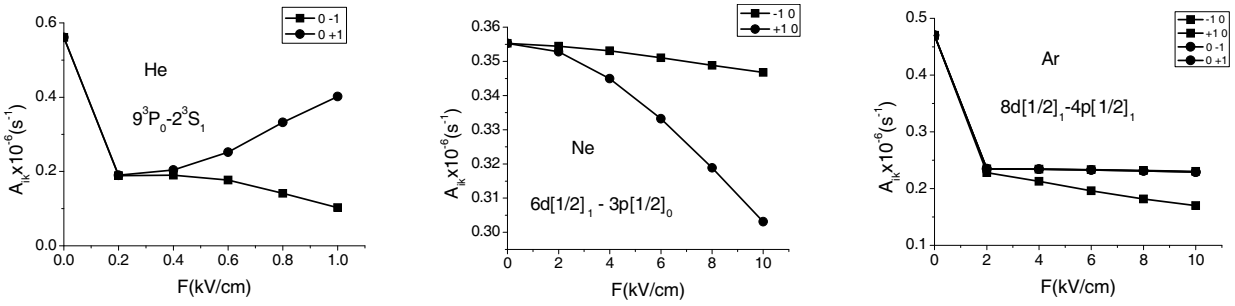

Figure 1: F-dependence of transition probabilities for states with $J,\ J' = 0,\ 1$ ($\omega = 100\,\mathrm{MHz}$).

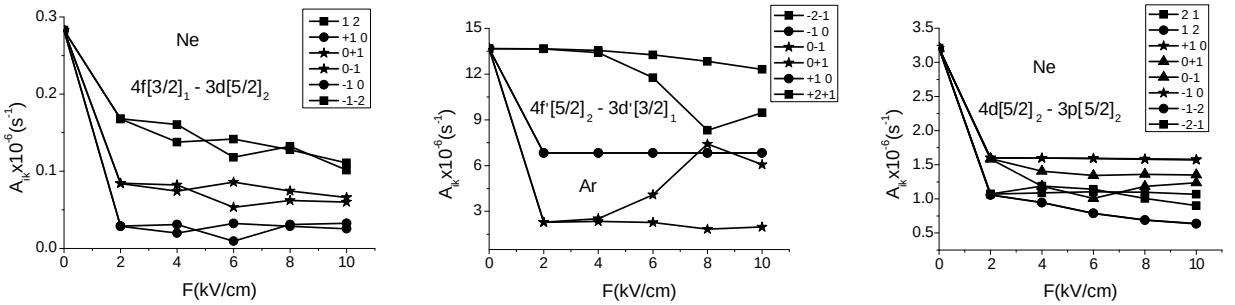

Figure 2: The F-dependence of transition probabilities for states with $J,\ J' = 1,\ 2$ ($\omega = 100\,\mathrm{MHz}$).

2) For weak mixture of the Stark states, the transition probabilities are practically indifferent to an increase in the electric field frequency. In particular, probabilities of the $5^3P_0(M = 0) - 2^3S_1(M' = \pm 1)$ transitions for the He atom are equal to $1.01 \cdot 10^6\,\mathrm{s}^{-1}$ at ω from 10^2 to $10^7\,\mathrm{MHz}$. Analogous results were obtained for other rare gas atoms. For strong state interactions, an increase in ω leads to the fact that unequiprobable $M \to M'$ transitions tend to become pairwise equiprobable (Fig. 3).

3) Both for weak and strong mixtures of states, the behavior of the $A(JM \to J'M')$ probabilities for $J \leq J'$ and $J > J'$ differs noticeably. If $J \leq J'$, then the probabilities of all transitions drastically diminish with switching on the electric field, and then they become practically insensitive to changes in the electric field strength. On the contrary, if $J > J'$, then at least one of all probabilities is practically independent of the electric field strength, whereas the remaining ones demonstrate the same behavior as that of the transition probabilities for $J \leq J'$ (see Table 1 and Figs. 1 and 2).

4) Both for weak and strong mixture of states, switching on the electric field leads to the M-ordered distribution of transition probabilities. As can be seen from Table 1 and Fig. 2, for the $J = 1 \to J' = 2$ transitions, the probabilities of the $\pm M \to \max|M'|$ transitions are maximal, and these probabilities decrease with M'. The same behavior is observed for the $J = 2 \to J' = 1$ transitions, namely, probabilities of the $\max|M| \to \pm M'$ transitions are maximal, and these probabilities decrease with M.

Thereby, the obtained results have allowed us to reveal the role of the electronic structure of

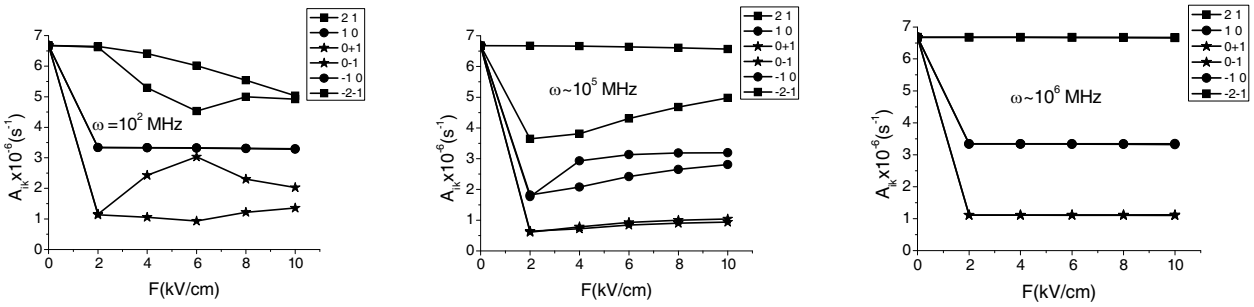

Figure 3: Ne atom. The ω-dependence for probabilities of the $4d[5/2]_2M$–$3p[3/2]_1M'$ transitions.

Table 1: Dependence of transition probabilities (in $10^6\,\mathrm{s}^{-1}$) on the electric field strength ($\omega = 100\,\mathrm{MHz}$).

Atom	Transition	λ (nm) (at $F=0$)	A_{ik} (at $F=0$)	$M \to M'$	A_{ik}	
					$F = 2\,\mathrm{kV/cm}$	$F = 10\,\mathrm{kV/cm}$
Ne	$9s'\ [1/2]_0$–$3p'[3/2]_1$	452.898	0.51	$0 \to \pm1$	0.17	0.17
Ar	$4p'[1/2]_1$–$4s'[1/2]_0$	772.663	12.51	$\pm1 \to 0$	12.50	12.50
Kr	$6p'\ [3/2]_1$–$5s'[1/2]_1$	430.170	1.57	$\pm1 \to 0$	1.57	1.57
				$0 \to \pm1$	1.57	1.57
Ne	$9s'[1/2]_1$–$3p'[3/2]_2$	454.577	0.436	$\pm1 \to \pm2$	0.173	0.131
				$\pm1 \to 0$	0.044	0.043
				$0 \to \pm1$	0.131	0.130
Ar	$4p[5/2]_2$–$4s[3/2]_1$	842.696	22.46	$\pm2 \to \pm1$	22.46	22.46
				$\pm1 \to 0$	11.23	11.23
				$0 \to \pm1$	3.75	3.75

atomic states in the behavior of transition probabilities in the electric field and to classify the behavior of transition probabilities according to the electronic structure of these states.

4. CONCLUSIONS

Based on our calculation results, the classification of the behavior of transition probabilities in emission spectra of rare gas atoms in an alternating circular electric field depending on the electronic structure of atomic states was established. The found classification gives a possibility to predict the behavior of spectral characteristics of atoms at changes in the electric field parameters.

These theoretical results obtained for the first time are interesting from the theoretical viewpoint and can be used for solving practical problems of plasma spectroscopy, gas discharge physics, and astrophysics.

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