

Computer simulation of ion emission spectra in alternating electric fields

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Abstract. The unified theoretical approach is developed for calculating the ion emission spectra in alternating electric fields. The suggested approach, based on numerical solution of the non-stationary Schrödinger equation, is free from limitations of perturbation theory and is valid in wide ranges of electric field strength and frequency. This approach has been implemented in a special software package IonStarkD written in FORTRAN and Maple. Wide potentialities of the proposed package are very useful in solving many practical problems of gas discharge physics, plasma diagnostics, astrophysics and all branches of physics, where one needs to investigate the influence of alternating electric fields on properties of the object of study.

Keywords: ion emission spectra, software package, spectroscopic characteristics.

1. Introduction

Spectroscopic methods play a significant role in the study of processes occurring in plasma and the estimation of the plasma parameters. The appearance of ions under excitation by external electric fields is observed quite quickly, therefore, modeling such spectra is a topical problem of modern physics. The influence of the electric field leads not only to the dynamic Stark effect, but also to the dependencies of the transition probabilities and the spectral line intensities on the electric field strength and frequency. To identify correctly the ion emission spectra excited by the electric field and to estimate accurately the spectroscopic characteristics of ions in this field, a reliable and efficient theoretical method is required.

After the first experiments in which the dynamic Stark effect was discovered, a theoretical approach based on the solution of the non-stationary Schrödinger equation within the framework of non-stationary perturbation theory has been developed sufficiently quickly ([1] and the references therein). But to date, many new excitation sources appear that generate electric fields in other, compared with lasers, strength and frequency ranges (light-emitting diodes, superpower lasers, etc.). By virtue of the complication of non-stationary perturbation theory and limitations inherent in it, this theory is not suitable for calculating the emission spectra in electric fields of the above-mentioned excitation sources.

In this work, the unified theoretical approach is suggested for calculating the ion emission spectra in alternating circularly polarized electric fields. This approach, based on numerical solution of the non-stationary Schrödinger equation, is free from limitations of perturbation theory and is valid in wide ranges of electric field strength and frequency. Sources generating circularly polarized electric fields are widely used in modern physics. In particular, electric fields of such polarization are generated in a high-frequency inductive discharge [2], lasers [3], and spin LEDs [4]. The suggested approach has been tested on rare gas ions, since these gases are widely used in various radiation sources and are often present in space plasma.

2. Calculation method

In calculations of the spectroscopic characteristics of ions in an alternating electric field, the wave functions and the energies of ions are determined by solving the non-stationary Schrödinger equation. In a circularly polarized electric field, the non-stationary Schrödinger equation is written as

$$i \frac{\partial \psi_n(\mathbf{r}, t)}{\partial t} = (H_0(\mathbf{r}) - F(x \cos \omega t \pm y \sin \omega t)) \psi_n(\mathbf{r}, t), \quad (1)$$

where $H_0(\mathbf{r})$ is the Hamiltonian of the unperturbed ion; F and ω are the strength and frequency of the electric field. In the case of the circular field polarization, the non-stationary Schrödinger equation specified by Eq. (1) can be transformed into the stationary one [5]. Such transformation can be carried out within the rotating-wave approximation [6]. In this approximation, the wave function in the coordinate system rotating about the Z -axis with the electric field frequency ω is written as

$$\varphi(\mathbf{r}, t) = \exp(i\omega t J_z) \psi(\mathbf{r}, t), \quad (2)$$

where J_z is the z -component of the total angular momentum operator. After substitution of the wave function specified by Eq. (2) into Eq. (1), we get the stationary Schrödinger equation

$$Q\varphi_n(\mathbf{r}) = \varepsilon_n \varphi_n(\mathbf{r}), \quad Q = (H_0 - \omega J_z \pm F D_x), \quad (3)$$

where Q is the time-independent operator of the energy of an ion in the electric field in the rotating coordinate system; ε_n and $\varphi_n(\mathbf{r})$ are the energy and wave function of the n th state of an ion in the electric field in the rotating coordinate system.

It should be noted that numerous attempts to solve Eq. (3) within the framework of stationary perturbation theory turned out to be unsuccessful by virtue of limitations of this theory and computational difficulties [5, 7]. Within the framework of the proposed method, Eq. (3) is solved by diagonalization of the energy matrix Q with the matrix elements calculated in the representation of unperturbed wave functions $\varphi_n^{(0)}$. In this case, the energies ε_n and the wave functions $\varphi_n(\mathbf{r})$, being solutions of the stationary Schrödinger equation (Eq. (3)), are determined by diagonalization of the energy matrix Q with elements

$$Q_{mn} = E_n^{(0)} \delta_{mn} - \omega \langle \varphi_m^{(0)}(\mathbf{r}) | J_z | \varphi_n^{(0)}(\mathbf{r}) \rangle \pm F \langle \varphi_m^{(0)}(\mathbf{r}) | D_x | \varphi_n^{(0)}(\mathbf{r}) \rangle, \quad (4)$$

$$\langle \varphi_m^{(0)} | D_x | \varphi_n^{(0)} \rangle = \langle \gamma J M | D_x | \gamma' J' M' \rangle = \frac{(-1)^{J-M}}{\sqrt{2}} \left[\begin{pmatrix} J & 1 & J' \\ -M & -1 & M' \end{pmatrix} - \begin{pmatrix} J & 1 & J' \\ -M & 1 & M' \end{pmatrix} \right] \langle \gamma J || D || \gamma' J' \rangle, \quad (5)$$

where $\varphi_n^{(0)}$ and $E_n^{(0)}$ are the wave function and the energy of the n th state of the ion in the absence of the electric field, and D_x is the x -component of the dipole moment operator. After diagonalization of the energy matrix Q , in the rotating coordinate system, the energies ε_n and the wave functions $\varphi_n(\mathbf{r})$ of the ion excited by the electric field are determined as

$$\varepsilon_n = \langle \varphi_n(\mathbf{r}) | Q | \varphi_n(\mathbf{r}) \rangle, \quad \varphi_n(\mathbf{r}) = \sum_k C_{nk} \varphi_k^{(0)}(\mathbf{r}). \quad (6)$$

Here C_{nk} are the expansion coefficients of the wave functions of the examined ion under the action of the electric field in terms of the unperturbed wave functions $\varphi_k^{(0)}(\mathbf{r})$. To return to the initial coordinate system, it is necessary to make average over the oscillation period of the electric field. After averaging, the wave functions and the average energies of the ion in the initial coordinate system are written as

$$\psi_n(\mathbf{r}, t) = \exp(-i(\omega J_z + \varepsilon_n)t) \sum_k C_{nk} \varphi_k^{(0)}(\mathbf{r}), \quad (7)$$

$$\bar{E}_n = \langle \psi_n(\mathbf{r}, t) | H(\mathbf{r}, t) | \psi_n(\mathbf{r}, t) \rangle = \varepsilon_n + \omega \langle \varphi_n(\mathbf{r}) | J_z | \varphi_n(\mathbf{r}) \rangle. \quad (8)$$

Then the wave functions and the energies specified by Eqs. (7) and (8) are used for calculating spectroscopic characteristics of ions, such as the positions of the Stark components of the spectral

lines, the transition probabilities between the Stark states of ions, and the Stark component intensities. The positions of the Stark components of the spectral lines are calculated as

$$\Delta E_{MM'} = (\bar{E}_{JM} - \bar{E}_{JM'}), \quad (9)$$

where the energy \bar{E}_{JM} of the Stark state JM is calculated using Eq. (8). The spontaneous transition probabilities between the Stark states JM and $J'M'$ are computed using the formula

$$A(JM \rightarrow J'M') = \frac{4\omega_{JM,JM'}^3}{3\hbar c^3} \sum_q \left| \sum_{ij} C_i^{(JM)} C_j^{(J'M')} (-1)^{J_i - M_i} \begin{pmatrix} J_i & 1 & J_j \\ -M_i & q & M_j \end{pmatrix} \langle \gamma_i J_i \| D \| \gamma_j J_j \rangle \right|^2, \quad (10)$$

where $C_i^{(JM)}$ and $C_j^{(J'M')}$ are the expansion coefficients from Eq. (6), and $\omega_{JM,JM'}$ is the frequency of the $JM \rightarrow J'M'$ transition. The reduced matrix elements $\langle \gamma J \| D \| \gamma' J' \rangle$ in Eqs. (5) and (10) are calculated using the following formulas

$$\langle \gamma J \| D \| \gamma' J' \rangle = A(-1)^q Q(T_1 T_2 J, U_1' U_2' J') \langle l \| r \| l' \rangle, \quad \langle l \| r \| l' \rangle = (-1)^{\frac{3l+l'+3}{2}} \sqrt{\max(l, l')} \langle R_{nl} | r | R_{n'l'} \rangle \quad (11)$$

$$\langle R_{nl} | r | R_{n'l'} \rangle = \int_0^\infty R_{nl}(r) r R_{n'l'}(r) r^2 dr, \quad (12)$$

where $T_1 T_2 J$ and $U_1' U_2' J'$ are the quantum numbers of the ion energy level within the LS or JJ coupling scheme. Calculation formulas for the multipliers A and $Q(T_1 T_2 J, U_1' U_2' J')$ from Eq. (11) are reported in [8]. The radial integral $\langle R_{nl} | r | R_{n'l'} \rangle$ in Eq. (12) is computed using our semiempirical formula, because the Bates–Damgaard method [9] is unsuitable for its calculation. The specific form of this semiempirical formula and details of its derivation are given in [10].

The Stark component intensities are calculated as

$$I(JM \rightarrow J'M') = N_{JM} A(JM \rightarrow J'M') \Delta E_{MM'}, \quad (13)$$

where N_{JM} is the population of the Stark state JM . The method for calculating populations N_{JM} is specified by the excitation mechanism of the spectrum.

It follows from the above reasoning that no one formula of the proposed theoretical approach has limitations on the parameters of the electric field inherent in perturbation theory. Moreover, since the diagonalization procedure is used to determine the energies and the wave functions of ions in the electric field, the interaction of all Stark states is taken into account automatically, whereas in perturbation theory, ion states are considered as isolated ones and theorists are forced to limit themselves to maximum four-level approximation. Therefore, the suggested numerical approach for calculating ion emission spectra in the electric field is free from limitations of perturbation theory and can be used for calculating these spectra in the electric field with the electric field strength and frequency changing in wide ranges.

3. Software package IonStarkD

The proposed theoretical approach has been implemented in a special software package IonStarkD written in FORTRAN and Maple. A flow diagram of this package is given in Fig. 1. As seen from this diagram, the package IonStarkD consists of three parts. In the first part of the package, the basis set of unperturbed energy states is constructed. The second part calculates the wave functions and the average energies of the examined ion in the electric field. The third part of the package computes different spectroscopic characteristics of the ion in the electric field using the wave functions and

the energies obtained in the second part. Let us consider these parts of the package IonStarkD in detail.

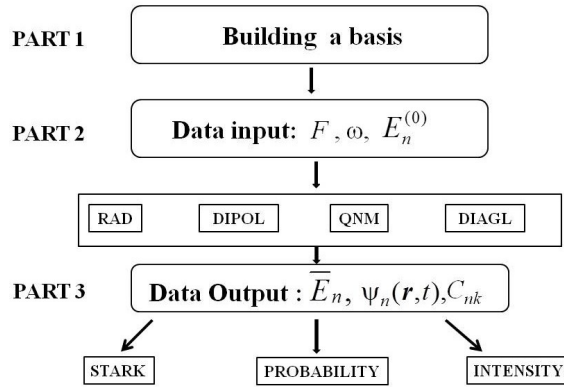


Fig. 1. Flow diagram of the software package IonStarkD.

3.1. Part 1 of the package IonStarkD. Programs for forming the basis set of unperturbed energy states of the ion under consideration

In calculations of the S -, P -, and D -states of rare gas ions, the LS coupling scheme is used. The F -states are calculated within the Jl coupling scheme. The verification of the convergence of the diagonalization procedure showed that to ensure the reliability of the calculations, the basis of unperturbed energies must include the nl -configurations with $n < 10$. Within the framework of the suggested theoretical approach, unperturbed ion energies are taken from the NIST database [11]. However, even this most complete database lacks for many energy terms. The missed energy terms needed for correct computations are calculated by the Hartree-Fock method using the Froese Fisher program [12]. In these calculations, the unperturbed energies $E_n^{(0)}$ are calculated taking into account all electrons of ions. The splitting of the energy terms caused by the spin-orbit interaction is performed within the framework of the formalism of irreducible tensor operators. A special program is written in Maple for calculating coefficients of the matrix elements of the spin-orbit interaction operator.

3.2. Part 2 of the package IonStarkD. Programs for calculation and diagonalization of the energy matrix of the ion in the electric field

All programs of this part are written in FORTRAN.

DATA INPUT: inputs the electric field parameters F and ω , and the positions of unperturbed energy levels with their quantum numbers for the examined ion. To input these data, a graphical user interface is used.

RAD: computes the radial integrals given by Eq. (12). The calculations of these integrals are performed using our efficient and fast technique (see Section 2).

DIPOL: computes the matrix elements of the D_x operator given by Eq. (11). To calculate the reduced matrix elements $\langle \gamma J \| D \| \gamma' J' \rangle$, additional programs for calculating the Clebsch-Gordan coefficients and the nj -symbols ($n = 3, 6, 9, 12$) is written.

QNM: computes the matrix elements of the energy matrix given by Eq. (4).

DIAGL: diagonalizes the energy matrix of the ion in the electric field. For decreasing calculation time, the energy matrix is reduced to a block type. Diagonalization procedure is thoroughly tested. As the criterion of the procedure accuracy the performance index τ is used. If the matrix equation

$$Ax = \lambda x, \quad (14)$$

is solved, then the performance index is defined to be

$$\tau = \max_{1 \leq j \leq n} \frac{\|A\tilde{x}_j - \tilde{\lambda}_j \tilde{x}_j\|}{10n\varepsilon \|A\| \cdot \|\tilde{x}_j\|}, \quad (15)$$

where $\|x\|$ is the norm of the vector x , ε is the machine precision, n is the order of the matrix A , $\tilde{\lambda}_j$ and \tilde{x}_j are approximate solutions of Eq. (14). The results of diagonalization procedure DIAGL are considered excellent, if $\tau \leq 1$, good if $1 \leq \tau \leq 100$, and poor if $\tau > 100$. Our tests have been shown that the performance index τ is 10^{-2} – 10^{-3} for $\omega = 10^2$ – 10^9 MHz, $F = 0.2$ – 500 kV/cm.

DATA OUTPUT. After execution of diagonalization procedure, we get the wave functions (see Eq. (7)) and the average energies (see Eq. (8)) of the ion in the electric field. Additionally, we have a special file with the expansion coefficients C_{nk} from Eq. (6), where the expansion coefficients are printed in descending order. These data allow the degree of the Stark state interactions to be estimated.

3.3. Part 3 of the package IonStarkD. Programs for calculating the AC Stark effect and the spectroscopic characteristics of ions in the electric field

The obtained output data (the wave functions and the average energies of the ion in the electric field) are further used to calculate the spectroscopic characteristics of this ion for the different values of F and ω .

STARK: computes the positions of the Stark components of ion spectral lines relative to the position of these lines in the absence of the electric field.

PROBABILITY: computes the spontaneous transition probabilities between the Stark states JM and $J'M'$ given by Eq. (10).

INTENSITY: computes the intensities of the Stark components of spectral lines given by Eq. (13). The programs STARK, PROBABILITY, and INTENSITY are written in FORTRAN.

4. Conclusion

The suggested software package IonStarkD is an efficient and reliable instrument for studying the ion emission spectra in alternating circularly polarized electric fields with the parameters changing in wide ranges. The results obtained by using this package allow one to identify correctly the ion energy spectra in the electric field as well as to estimate the plasma parameters such as strength and frequency of the electric field inside the discharge and the plasma temperature. Additionally, the simulation of the ion spectra with the package IonStarkD makes it possible to analyze the role of the electric field in the processes of increasing/decreasing of the spectral line intensities.

Wide potentialities of the suggested package are very useful in solving many practical problems of gas discharge physics, plasma diagnostics, astrophysics and all branches of physics, where one needs to investigate the influence of alternating electric fields on properties of the object of study. Finally, the software package IonStarkD can be very useful for developing new radiation sources and for searching the optimal operating mode of already existing radiation sources.

5. References

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