Numerical method for calculating atomic spectra in strong laser fields

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Abstract. In this paper, a new theoretical method is suggested for calculating atomic emission spectra in strong laser fields. This numerical method based on diagonalization of the energy matrix of an atom in the electric field is free from limitations of perturbation theory and valid for a wide range of changes in the electric field strength and frequency. Within the framework of the suggested method, the ground-state shifts of He, Ne, Ar, and Kr atoms in a circularly polarized electric field are computed. Calculations are carried out for electric fields with strengths of 0.06 and 0.15 a.u. and frequencies from $10^{-4}$ to 0.057 a.u. In addition, the effect of ordering of the transition probabilities with respect to the magnetic quantum number $M$ in the electric field is also investigated. The results obtained can be useful for correct interpretation of the experimental data and prediction of the behaviour of atomic emission spectra in strong laser fields.

1. Introduction
The influence of laser fields on atoms leads to an appearance of emission spectra specified by bound-bound transitions and electronic spectra arising due to ionization of atoms. For correct interpretation of these spectra, one needs accurate calculation methods, and non-stationary perturbation theory is one of them. In spite of limitations of perturbation theory (not very strong electric fields, isolated atomic energy levels, and Rydberg atoms [1]), most of the experimental data obtained for low-power optical lasers were explained within this theory ([2] and the references therein). However, by the present time, a lot of other excitation sources (in particular, electrodeless high-frequency lamps, light-emitting diodes, and superpower lasers) have appeared. These sources generate electric fields with parameters essentially different from those of optical lasers. In such cases, when non-stationary perturbation theory is unsuitable by virtue of its limitations, one needs a new reliable and efficient theoretical method for calculating atomic emission spectra in electric fields.

As for theoretical study of influence of strong laser fields on atoms and ions, the pioneer work in this brunch of physics was Keldysh’s work [3]. In this work, the theory and methods for calculating tunnel and multiphoton ionizations in strong laser fields were suggested. After this work, many scientific papers were devoted to these problems (see, for example, reviews [4–6] and the references therein). It should be noted that the main attention in these works was paid to ionization processes in atoms (e.g., to the bound-free transitions) under the influence of alternating electric fields, but processes caused by the bound-bound transitions, as a rule, were neglected, because these probabilities were considered to be too small. However, at present time, calculating the discrete atomic spectra and the bound-bound transition probabilities in strong laser fields is also a vital problem. Firstly, shifts and
splitting of atomic energy levels induced by the non-resonant dynamic Stark effect always lead to an appearance of the so-called dynamic resonances [7]. Secondly, the ground-state energy shifts in the electric fields are necessary for the refinement of formulas for calculating the ionization rates of the ground states of rare gas atoms derived in [8, 9]. Moreover, because the ground states of rare gas atoms are not Rydberg ones, calculations of their shifts in the electric field necessitate the consideration of interactions between the Stark states [10]. Finally, from the theoretical viewpoint, it is very interesting to reveal some regularities in the behaviour of the ionization rates and the bound-bound transition probabilities in an electric field and to understand reasons for these regularities.

In the present work, a theoretical method free from limitations of perturbation theory is used for calculating rare gas emission spectra in strong circularly polarized laser fields that allows one to take into account the Stark state interactions. This numerical method suggested and developed by us in [11, 12] is based on diagonalization of the energy matrix of an atom in electric fields. It gives one the possibility of calculating emission spectra of any atoms in alternating circularly polarized electric fields with strength and frequency changing in wide ranges.

Previously, the suggested numerical method was applied to calculate emission spectra of rare gas atoms in alternating circularly polarized electric fields with the electric field strength changing from 0 to 150 kV/cm and electric field frequency changing in the range $10^3–10^8$ MHz [13–15]. The calculation results are in excellent agreement with the available theoretical and experimental data, in particular, with [16]. The results obtained stimulated our interest to calculation of the ground-state shifts and the bound-bound transition probabilities of rare gas atoms in strong low-frequency laser fields by the method of energy matrix diagonalization of an atom in the electric field, because the conditions of applicability of perturbation theory are violated for such electric fields.

In Section 2 of the present work we describe the method of energy matrix diagonalization of an atom in the electric field. In Section 3 we check the validity of the suggested numerical method and investigate its convergence in calculations of the ground-state shifts of rare gas atoms in laser fields with different values of the electric field parameters. Then, in Section 3, we study a very interesting effect of ordering of the bound-bound transition probabilities with respect to the magnetic quantum number $M$ and discuss the presence of the same $M$-ordering for the bound-free transition probabilities.

2. Theoretical method

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

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

(1)

where $\psi_n$ is the wave function of the $n$-th state of the system, $H_0$ 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 electric field of frequency $\omega$ and strength $F$. The “+” and “−” signs correspond to the right and left polarization of the field, respectively. For the case of a circularly polarized field, the non-stationary Schrödinger equation can be reduced to the stationary one due to separation of spatial and time variables within the framework of the rotating-wave approximation [17].

Within this approximation, the wave function in the coordinate system rotating about the Z-axis with the frequency $\omega$ has the form

$$\varphi(r,t) = \exp(i \omega J_z)\psi(r,t),$$  

(2)

where $J_z$ is the $z$-component of the total angular momentum operator. On substituting equation (2) in equation (1), we get

$$i \frac{\partial \varphi(r,t)}{\partial t} = Q \varphi(r,t), \quad Q = (H_0 - \omega J_z \pm FD_z).$$  

(3)

As seen from equation (3), the operator $Q$ 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 have
\[ Q \varphi(r) = e \varphi(r), \quad \varphi(r, t) = \exp(-i \varepsilon t) \varphi(r), \]  

where \( Q \) is the energy operator of an atom in the electric field, and \( \varepsilon \) and \( \varphi(r, t) \) are the energy and wave function of an atom in the electric field in the rotating coordinate system. It is obvious that the Schrödinger equation (4) can be solved within stationary perturbation theory, but this way of solution has been found too complicated [18, 19]. We found that instead of solving the Schrödinger equation (4) within perturbation theory, it is much more convenient to solve it using diagonalization procedure. It was shown that the wave functions and energies of an atom, being solutions to the Schrödinger equation (4), are found from diagonalization of the energy matrix of an atom in the electric field with the following elements

\[ Q_{\mu \nu} = E_n^{(0)} \delta_{\mu \nu} - \omega < \varphi_n^{(0)}(r) | J_z | \varphi_n^{(0)}(r) > \pm F < \varphi_n^{(0)}(r) | D_x | \varphi_n^{(0)}(r) >. \]  

This matrix is obtained in the coordinate system rotating about the Z-axis with frequency \( \omega \). In equation (5), \( \varphi_n^{(0)} \) and \( E_n^{(0)} \) are the wave function and energy of the \( n \)-th state of an atom in the absence of the electric field; \( J_z \) is the \( z \)-component of the total angular momentum operator; and \( D_x \) is the \( x \)-component of the dipole moment operator. Upon diagonalization of the energy matrix with elements (5), we get the energies \( \varepsilon_n \) and wave functions \( \varphi_n \) as

\[ \varphi_n(r, t) = \exp(-i \varepsilon_n t) \sum_k C_{nk}(F, \omega) \varphi_k^{(0)}(r) \]  

for the \( n \) atomic states in the electric field in the rotating coordinate system. The coefficients \( C_{nk} \) in the wave function (6) are the expansion coefficients of the wave functions of an atom under the action of the electric field strength and frequency.

To go to the initial coordinate system and find the average atomic energies in the electric field, it is necessary to perform averaging over the oscillation period. After averaging over the oscillation period, the wave functions and average energies of an atom in the electric field in the initial coordinate system are written as

\[ \psi_n(r, t) = \exp(-i(\omega J_z + \varepsilon_n) t) \sum_k C_{nk}(F, \omega) \varphi_k^{(0)}(r), \]  

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

It follows from equation (8) that \( \bar{E}_n \) is time-independent.

The wave functions and energies of an atom in the electric field specified by equations (7) and (8) are further used for calculating spontaneous transition probabilities between the Stark states \( JM \) and \( JM' \). These transition probabilities are computed using the formula

\[ A(JM \rightarrow JM') = \frac{4 \omega_{JM, JM'}^3}{3 \hbar c^3} | D_{JM, JM'} |^2, \]

\[ | D_{JM, JM'} |^2 = \sum_{s, t} C_s^{JM} C_t^{JM'} (-1)^{s-t} \left( \begin{array}{c c c c} J_i & 1 & J_i & 1 \\ -M_i & q & M_j & \end{array} \right) < \gamma_s J_i \| D \| \gamma_t J_j >^2, \]

where \( C_s^{JM} \) and \( C_t^{JM'} \) are the expansion coefficients from equation (7), and \( \omega_{JM, JM'} \) is the frequency of the \( JM \rightarrow JM' \) transition.

The matrix elements of the \( D \) operator in equations (5) and (10) are determined as

\[ < \varphi_n^{(0)} | D_j | \varphi_n^{(0)} >= \gamma^{JM} | D_j | \gamma^{JM'} > = \frac{(-1)^{s-M}}{2} \left( \begin{array}{c c c c} J_i & 1 & J_i & 1 \\ -M_i & q & M_j & \end{array} \right) < \gamma^{JM} | D | \gamma^{JM'} >, \]

where the reduced matrix elements \( \gamma^{JM} | D | \gamma^{JM'} > \) are calculated depending on a coupling scheme. The reduced matrix elements \( \gamma^{JM} | D | \gamma^{JM'} > \) are computed using the following formulas
\[
<\mathcal{W}|V_{\ell'\ell''}|\mathcal{W}'> = (\mathcal{A})|Q(T_1T_2J,U|U_1'U_2'J')<\mathcal{W}|, \quad (12)
\]
\[
<\mathcal{W}| = (-1)^{\,\frac{\ell'+\ell''+1}{2}} \max(l,l') < R_{nl} | R_{n'l'} > , \quad (13)
\]
\[
< R_{nl} | R_{n'l'} > = \int_0^\infty R_{nl}(r)R_{n'l'}(r)r^2 dr , \quad (14)
\]

where \(T_1T_2J\) and \(U|U_1'U_2'J'\) are the quantum numbers of the atomic energy level within the corresponding coupling scheme; \(nl\) and \(n'l'\) are the quantum numbers of the optical electron, which goes from the state \(nl\) to the state \(n'l'\). The calculation formulas for the multipliers \(Q(T_1T_2J,U|U_1'U_2'J')\) from equation (12) were reported in [20]. The radial integral \(< R_{nl} | R_{n'l'} >\) in equation (14) is calculated using a semiempirical formula, which is an improved modification of the Bates-Damgaard formula [21]. The specific form of our semiempirical formula for computation of the radial integrals and details of its derivation were reported in [12].

It follows from the above reasoning that the proposed theoretical approach is free from limitations of perturbation theory and can be used for calculating the dynamic Stark effect in a circularly polarized electric field with the strength and frequency changing in wide ranges. Since the energies and wave functions in the electric field are determined by the diagonalization procedure, it allows us to take into account the interaction of the Stark states. The algorithm of the developed theoretical approach is implemented in a special software package StarkD written in FORTRAN.

3. Results and discussion
In this work, the suggested theoretical approach was applied to calculate the energy spectra of rare gas atoms in strong alternating circularly polarized electric fields of different strengths and frequencies. First of all, it is necessary to check the validity of our numerical method for strong laser fields.

It is well known that the use of any theoretical methods with expansions in some basis functions requires an investigation of the convergence of the calculation results with increasing basis. The convergence problem is very complicated, and it must be solved in each individual case. In particular, in perturbation theory, the energy level shifts induced by the electric field are proportional to the atomic dynamic polarizability [1]. The convergence of the basis in calculating atomic polarizabilities was discussed in classical monographs [1, 19]. The detailed investigation of the basis convergence was performed in [10], where atomic polarizabilities were computed by the method of the reduced-added Green function.

The method of energy matrix diagonalization of an atom in the electric field used in the present work is also based on calculating atomic characteristics with the wave functions being the expansions in the basis set of unperturbed wave functions. It was shown in [11], for the electric fields with parameters \(F = 0–10\) kV/cm and \(\omega = 10^2–10^8\) cm\(^{-1}\), the inclusion of unperturbed wave functions \(\phi_{nl}^{(0)}\) with \(l = 0–3\) and \(n \leq 10\) in the basis set (the basis \(N_0\)) allows us to achieve convergence of calculations of atomic energies in the electric field. In case of strong laser fields, our calculation results showed that in order to achieve the calculation convergence, it is necessary to increase the basis set. Firstly, we have found that it is necessary to include the one-electron functions \(\phi_{nl}^{(0)}\) with \(l = 4\) in the basis set \(N_0\) (the basis \(N_1\)). Secondly, the one-electron functions \(\phi_{nl}^{(0)}\) with the principal quantum number \(n \leq 15\) also must be added to the basis set \(N_1\) (the basis \(N_2\)).

As an illustration of the convergence of our calculation method with increasing basis set, the computed ground-state energy shifts for rare gas atoms in comparison with other theoretical data [1] are listed in table 1. These calculations were carried out for the shifts in the electric field of the neodymium laser (laser intensity of 30 MW/cm\(^2\) and \(\omega = 18800\) cm\(^{-1}\)).

As follows from table 1, the sign of our calculated shifts is negative that agrees with the computation results [1] obtained within the framework of perturbation theory. In addition, the calculation results from table 1 demonstrate the convergence of our numerical method with increasing
basis set. It should be noted that a further increase in the basis set has a weak influence on the shift value. As a whole, our computation data are in good agreement with the results presented in [1] except the ground-state shift of the Ne atom. The above-indicated difference is caused by the fact that in [1] the calculated value of the polarizability of the neon atom was $\alpha_n(\omega) = 5.25$ a.u., whereas at $\omega = 0.0$ a.u., the experimental value of the polarizability was $2.669$ a.u. [22], and at $\omega = 0.2$ a.u., $\alpha_n(\omega)$ equals $2.814$ a.u. [10] or $2.794$ a.u. [23].

**Table 1.** Ground-state energy shifts $\Delta E$ (in $10^{-3}$ cm$^{-1}$) for rare gas atoms in the Nd-laser field.

| $\Delta E$ | He  | Ne  | Ar  | Kr  |
|------------|-----|-----|-----|-----|
| $N_0$      | -0.032 | -0.061 | -0.262 | -0.391 |
| $N_1$      | -0.054 | -0.098 | -0.491 | -0.674 |
| $N_2$      | -0.059 | -0.108 | -0.544 | -0.793 |
| [1]        | -0.067 | -0.240 | -0.602 | -0.850 |

Then, our suggested theoretical approach was applied to calculate the energy spectra of rare gas atoms in alternating circularly polarized electric fields of strengths $F = 0.06$ a.u. and $F = 0.15$ a.u. at different values of the electric field frequency. First of all, the calculations of these shifts were computed at the electric field frequency $\omega = 10^{-4}$ a.u. to verify the convergence of our method. The results of these calculations are listed in table 2. As follows from this table, an increase in the set functions leads to the convergence of our calculation results. The signs of all ground-state energy shifts are negative and these shifts increase with atomic nuclear charge. The results obtained also agree with estimations of perturbation theory, and this fact confirms once more the validity of our numerical method.

**Table 2.** Ground-state energy shifts $\Delta E$ (in a.u.) for rare gas atoms in the circularly polarized electric fields ($\omega = 10^{-4}$ a.u.).

| $\Delta E$ | Ne  | Ar  | Kr  |
|------------|-----|-----|-----|
| $N_0$      | -0.0025 | -0.0075 | -0.0117 |
| $N_1$      | -0.0038 | -0.0112 | -0.0249 |
| $N_2$      | -0.0041 | -0.0127 | -0.0303 |
| [1]        | -0.00191 | -0.00702 | -0.00867 |

In addition, we also calculated the ground state shifts of rare gas atoms in strong laser field with the electric field strength $F = 0.15$ a.u. and frequency $\omega = 0.05$ a.u. The results obtained with the basis set $N_2$ are listed in table 3.

**Table 3.** Ground-state energy shifts $\Delta E$ (in a.u.) for rare gas atoms in the circularly polarized electric field with parameters $F = 0.15$ a.u. and $\omega = 0.05$ a.u.

| $\Delta E$ | Ne  | Ar  | Kr  |
|------------|-----|-----|-----|
| This work  | -0.0381 | -0.1229 | -0.2277 |
| [10]       | -0.0308 | -0.1212 | -0.2029 |

As follows from this table, the values of shifts of atomic ground states computed by our method are slightly greater than the calculation results presented in [10]; however, as a whole, our results are in good agreement with the calculation data [10].

It is well known that in the case of one-photon ionization, the ionization rate of the bound state depends on its quantum number $m$. For transitions with increasing angular momentum of the electron, the states with $m > 0$ are depleted faster than those with $m < 0$. Since both the bound-free and bound-
bound transitions are induced by the electric field, this suggests that the bound-bound transition probabilities between the Stark states \( JM \) will demonstrate a similar dependence on the magnetic quantum number \( M \). Actually, we have found that switching on the electric field leads to the \( M \)-ordering of the transition probabilities, and this effect has a global character.

In relatively weak circularly polarized electric fields, the bound-bound transition probabilities are ordered with respect to the magnetic quantum number \( M \) of the optical electron, and this regularity is valid in a wide range of changes in the electric field strength and frequency. As an illustration, figure 1 shows an evolution of probabilities of the \( nd^3D_2–2p^1P_1 \) transitions with increasing electric field strength for the He atom. In this figure and following figures, the magnetic quantum numbers \( M, M' \) of the \( JM \rightarrow JM' \) transitions are pointed in the frame. As can be seen from this figure, switching on the electric field leads to ordering of transition probabilities with respect to the magnetic quantum number \( M \), e.g., probabilities of the \( \max |M| \rightarrow \pm M' \) transitions are maximal, and these probabilities diminish with \( M \). This effect is observed for the electric field strength from 0 to 120 kV/cm (see figure 1).

![Figure 1. Dependence of transition probabilities between the Stark states on the electric field strength for the He atom: a) \( \omega = 10^2 \) MHz, b) \( \omega = 10^3 \) MHz.](image)

The \( M \)-ordering of transition probabilities is also detected for other rare gas atoms in the electric field. For example, the behaviour of the transition probabilities depending on the electric field strength for neon and argon atoms is shown in figure 2.

![Figure 2. Dependence of transition probabilities between the Stark states of rare gas atoms on the electric field strength at \( J > J' \) (\( \omega = 10^2 \) MHz).](image)
\[\pm M \rightarrow \max|M'| \text{ transitions have maximal values, and these probabilities diminish with } M'. \text{ Figure 3 is an obvious illustration of this fact.}\]

Finally, our calculation results have shown that the \(M\)-ordering of transition probabilities \(A(JM \rightarrow J'M')\) is observed for all rare gas atoms in alternating circularly polarized electric fields with frequencies changing from \(10^2\) to \(10^8\) MHz. As an illustration, figure 4 shows an evolution of probabilities of the \(6d_{5/2} - 5p_{3/2}\) transitions with increasing electric field frequency for the Kr atom. The examined frequencies are the electric field frequencies of different lasers, namely: \(\omega = 3.4352 \times 10^6\) MHz (an HCN laser), \(\omega = 2.4181 \times 10^7\) MHz (a \(\text{CO}_2\) laser), and \(\omega = 2.8301 \times 10^8\) MHz (a Nd laser).

**Figure 3.** Dependence of transition probabilities between the Stark states of rare gas atoms on the electric field strength for \(J < J'\) (\(\omega = 10^2\) MHz).

**Figure 4.** Dependence of transition probabilities between the Stark states on the electric field frequency for the \(6d_{5/2} - 5p_{3/2}\) transition of the Kr atom:
- HCN: \(\omega = 3.4352 \times 10^6\) MHz,
- \(\text{CO}_2\): \(\omega = 2.4181 \times 10^7\) MHz,
- Nd: \(\omega = 2.8301 \times 10^8\) MHz.
It is seen from our calculation results that the M-ordering of transition probabilities has a global character, because it is detected for all rare gas atoms influenced by electric fields. Owing to a global character of the $M$-ordering of transition probabilities $A(JM \rightarrow J'M')$, it is possible to assume that the above-described effect will take place in atomic emission spectra in strong laser fields. Our calculation results listed in table 4 confirm this assumption. As follows from this table, in strong laser fields the bound-bound transition probabilities are also $M$-ordered, and the probabilities of transitions between the Stark states with $M > 0$ are greater than those with $M < 0$ by analogy with the ionization rates.

| Transition $M \rightarrow M'$ | 1→2 | 1→0 | 0→1 | −1→2 | −1→0 | 0→1 |
|-----------------------------|------|------|------|-------|-------|------|
| Ne, $3p[1/2]_1→3s[3/2]_2$  | 2.58 | 2.5  | 1.17 | 2.08  | 0.21  | 0.35 |
| Ar, $5p[1/2]_1→5s[3/2]_2$  | 7.00 | 5.25 | 1.59 | 3.52  | 3.50  | 1.55 |

Thereby, based on our calculation results, we can conclude that the influence of strong circularly polarized laser fields leads to the $M$-ordering of both the bound-bound transition probabilities and the ionization rates of the Stark states of rare gas atoms, and this ordering has the same character.

4. Conclusions
The suggested theoretical approach can be useful for calculations of the excitation and ionization processes of atoms in strong laser fields when perturbation theory is inapplicable. Atomic spectra in the electric field obtained within the framework of our method has allowed us to reveal dynamic resonances arising in strong laser fields owing to the non-resonant Stark effect and to define the ground-state energy shifts in the electric fields needed for refinement of the formulas for calculating the ionization rates of the ground states of rare gas atoms. Finally, the calculations of the bound-bound transition probabilities are of interest for the study of the influence of electric fields on atoms when the bound-bound and bound-free transition probabilities are of the same order.

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