SOVIET PHYSICS JETP VOLUME 34, NUMBER 3 MARCH, 1972

PERTURBATION THEORY FOR THE MULTIPHOTON IONIZATION OF ATOMS

B. A. ZON, N. L. MANAKOV, and L. P. RAPOPORT

Voronezh State University

Submitted March 24, 1971

Zh. Eksp. Teor. Fiz. 61, 968–975 (September, 1971)

A method is proposed for summing the perturbation theory series which describe the probability for multiphoton ionization of atoms. The method is based on the utilization of the Green's function of an optical electron in a complex atom, this function being constructed within the framework of the approximation of the method of the quantum defect. Numerical calculations are carried out for three-photon ionization by linearly- and circularly-polarized light of the ground and metastable levels in hydrogen and of the metastable singlet and triplet levels in helium.

1. INTRODUCTION

At the present time multiphoton ionization of atoms is being intensively investigated both theoretically as well as experimentally (see the review article [1]). In this connection it turns out that the probability of the process is essentially determined by the structure of the particular atom involved.[2,3] This is easy to understand physically since for external electromagnetic fields which are smaller than the intratomic field, quasi-stationary excited states exist in the atom, and therefore the cross section for multiphoton ionization has a characteristic resonance structure. The internal structure of the atom is taken into account naturally during the calculation of the probability for the process according to perturbation theory.

Such calculations of the cross section for multiphoton ionization of the hydrogen atom, carried out in articles [4,5], are widely known. In these articles the Schwartz-Tiemann method[6] is used to calculate the amplitude for the process by means of numerical integration of a system of inhomogeneous differential equations of the first order. However, within the framework of this method the calculations turn out to be rather complicated, which may be one of the reasons for the substantial discrepancy between the results of article [5] and the results obtained by other authors.[7]

A number of approximate methods have been proposed for calculating the ionization of complex ions; in these methods an averaging of the energy denominators[8] or of the numerators (of the oscillator strengths) [9] was carried out in the infinite repeated series of perturbation theory. Bebb[10] calculated the indicated series for alkali atoms by summing some of the "principal" terms. In this connection the oscillator strengths were determined in the Coulomb approximation of Bates and Damgaard.

We have previously proposed a method for calculating the two-photon ionization of hydrogen, which is based on the use of the Coulomb Green's function; our method gave the possibility to derive an analytic expression for the amplitude for this process.[11] In the present article this method is generalized to the case of multiphoton ionization of complex atoms by using the Green's function of an optical electron in the quantum defect method (QDM), which is constructed in [12], instead of the Coulomb Green's function. Such an approach makes it possible to sum the infinite series of perturbation theory, including the continuous spectrum. Here the actual spectrum of the atom is taken into account exactly (the poles of the Green's function agree with the experimental spectrum), and the radial part of the Green's function is constructed out of regular and irregular Coulomb functions since, as is well known, in electric dipole transitions the regions far away from the atomic core give the major contributions to the integrals, and far away from the core the single-particle potential of the optical electron can be regarded as a Coulomb potential.

Thus, in the proposed work a consistent method of calculating multiphoton ionization is constructed within the framework of the QDM, which satisfactorily describes single-photon processes in atoms; the method is based on a single assumption about the weakness of the external electromagnetic field in comparison with the intratomic field. A systematic comparison of the predictions of the theory with the experimental data enables us to indicate the limits of applicability of the QDM for the calculation of multiphoton atomic processes. In addition, this enables us to determine the critical fields at which perturbation theory ceases to work. The latter is especially important since the question of the applicability of perturbation theory to multiphoton ionization processes has been discussed in the literature for a long time.

2. THE PROBABILITY FOR MULTIPHOTON IONIZATION

To the first nonvanishing order in perturbation theory, the probability for N-photon ionization has the following form in the nonrelativistic dipole approximation:[1]

$$\frac{dw_{nl_i}^{(N)}(\omega)}{d\Omega} = 2\pi\left(\omega\frac{F}{F_0}\right)^N |K_{fi}^{(N)}(\omega)|^2, \tag{1}$$

where

$$K_{fi}^{(N)}(\omega) = \langle f|(\boldsymbol{\varepsilon}\mathbf{r}_N)G_{E_i+(N-1)\omega}(\mathbf{r}_N, \mathbf{r}_{N-1})(\boldsymbol{\varepsilon}\mathbf{r}_{N-1})\ldots G_{E_i+\omega}(\mathbf{r}_2, \mathbf{r}_1)(\boldsymbol{\varepsilon}\mathbf{r}_1)|i\rangle,$$

$$|i\rangle = R_{nl_i}(r)Y_{l_i m_i}(\mathbf{r}),$$

---

[1] The atomic system of units is used in this article.

$$|f\rangle = \sum_{LM} i^L e^{i\eta_L} R_L(k;\, r)\, Y_{LM}(\mathbf{r})\, Y_{LM}^*(\mathbf{k}),$$

ω and ϵ denote the frequency and polarization of the incident photons; F denotes the photon flux in units of $\mathrm{cm}^{-2}\,\mathrm{sec}$; $F_0 = c/2\pi a^3 = 3.22 \times 10^{34}\ \mathrm{cm}^{-2}\,\mathrm{sec}$; a is the Bohr radius; n, l_i, m_i are the quantum numbers of the electron in the initial state; $R_L(k;\, r)$, η_L, k are the radial function, phase, and wave vector of the outgoing electron; $G_E(\mathbf{r}, \mathbf{r}')$ is the Green's function of the optical electron, which is determined as the following summation over the complete set of single-particle intermediate states:

$$G_E(\mathbf{r}, \mathbf{r}') = \sum_{\lambda} \frac{\langle \mathbf{r}|\lambda\rangle \langle\lambda|\mathbf{r}'\rangle}{E_\lambda - E}.$$

The function $G_E(\mathbf{r}, \mathbf{r}')$ was constructed in the approximation of the QDM in [12], and for $E > 0$ it has the form

$$G_E(\mathbf{r}, \mathbf{r}') = \sum_{lm} g_l(E;\, r, r')\, Y_{lm}(\mathbf{r})\, Y_{lm}^*(\mathbf{r}'), \tag{2}$$

where

$$g_l(E;\, r, r') = \frac{\nu}{rr'} e^{i\pi\nu} \Big[e^{2i(\eta_l - \pi l/2)} W_{\nu,\, l+1/2}\left(\frac{2r}{\nu}\right) W_{\nu,\, l+1/2}\left(\frac{2r'}{\nu}\right)$$
$$- W_{-\nu,\, l+1/2}\left(-\frac{2r_<}{\nu}\right) W_{\nu,\, l+1/2}\left(\frac{2r_>}{\nu}\right)\Big],$$
$$\eta_l = \sigma_l + \delta_l, \quad \sigma_l = \arg\Gamma(l + 1 - \nu),$$

δ_l denotes the phase of the l-th partial wave associated with the non-Coulomb part of the potential, $\nu = (-2E)^{-1/2}$, W is the Whittaker function, and $r_>(r_<)$ denotes the larger (smaller) of the quantities r and r′.

Let us use the relation between the complex functions W and the Coulomb wave functions $F_l(k;\, r)$ and $G_l(k;\, r)$:[13]

$$W_{\pm\nu,\, l+1/2}\left(\pm\frac{2r}{\nu}\right) = (\pm i)^{l+1} e^{\mp i\sigma_l + \pi/2k} [F_l(k;\, r) \mp iG_l(k;\, r)],$$
$$k = i/\nu = \sqrt{2E}.$$

This makes it possible to derive explicit expressions for the real and imaginary parts of the function g_l:

$$\operatorname{Im} g_l(E;\, r, r') = -\frac{2}{krr'}\{F_l(k;\, r)\cos\delta_l(E) + G_l(k;\, r)\sin\delta_l(E)\}\cdot$$
$$\cdot\{F_l(k;\, r')\cos\delta_l(E) + G_l(k;\, r')\sin\delta_l(E)\}, \tag{3}$$

$$\operatorname{Re} g_l(E;\, r, r') = \frac{-2}{krr'}\{F_l(k;\, r_<)G_l(k;\, r_>) - \sin^2\delta_l(E)\,[F_l(k;\, r)G_l(k;\, r')$$
$$+ G_l(k;\, r)F_l(k;\, r')] + {}^1\!/_2 \sin 2\delta_l(E)\,[G_l(k;\, r)G_l(k;\, r')$$
$$- F_l(k;\, r)F_l(k;\, r')]\}. \tag{4}$$

Expression (3) can be rewritten in the form

$$\operatorname{Im} g_l(E;\, r, r') = -\pi R_l(k;\, r) R_l(k;\, r'), \tag{5}$$

where

$$R_L(k;\, r) = \sqrt{\frac{2}{\pi k}}\,\frac{1}{r}\{F_L(k;\, r)\cos\delta_L(E) + G_L(k;\, r)\sin\delta_L(E)\} \tag{6}$$

is the radial wave function of the continuous spectrum in the QDM, normalized on the energy scale, and having the asymptotic form

$$R_L(k;\, r) \xrightarrow[r\to\infty]{} \sqrt{\frac{2}{\pi k}} \sin\left(kr + \frac{\ln 2kr}{k} + \delta_L + \sigma_L - \frac{L\pi}{2}\right).$$

With the aid of the derived formulas one can easily verify that the optical theorem is satisfied in the proposed approach. In fact, the amplitude for the scattering of light at zero angle is given by

$$f(0) = (\alpha\omega)^2 \alpha_n(\omega),$$

where

$$\alpha_n(\omega) = \langle n|\,(\epsilon\mathbf{r})\,\{G_{E_n+\omega}(\mathbf{r}, \mathbf{r}') + G_{E_n-\omega}(\mathbf{r}, \mathbf{r}')\}\,(\epsilon\mathbf{r}')\,|n\rangle \tag{7}$$

denotes the polarizability of the n-th atomic level and $\alpha = 1/_{137}$. Since the Green's function G_E is real for $E < 0$, then for the case under consideration $\omega > |E_n|$ and by using Eq. (5) we obtain the optical theorem:

$$\operatorname{Im} f(0) = \frac{\pi(\alpha\omega)^2}{3(2l+1)} \sum_{L = l\pm 1} l_{max} \left| \int_0^\infty r^3 R_{nl}(r) R_L(k;\, r)\, dr \right|^2 = \frac{\alpha\omega}{4\pi}\sigma_{nl}(E_n + \omega), \tag{8}$$

where $\sigma_{nl}(E_n + \omega)$ denotes the cross section for one-photon ionization, $l_{max} = \max(L, l)$. In the QDM approximation the Green's function $g_l(E;\, r, r')$ has the following form[12] for $E < 0$:

$$g_l(E;\, r, r') = \frac{\nu}{rr'}\Big[\frac{\Gamma(l+1-\nu)}{\Gamma(2l+2)} M_{\nu,\, l+1/2}\left(\frac{2r_<}{\nu}\right) W_{\nu,\, l+}\left(\frac{2r_>}{\nu}\right)$$
$$+ \frac{\Gamma(l+1-\nu)}{\Gamma(l+1+\nu)}\,\frac{\sin\pi(\mu_l(E) + l)}{\sin\pi(\mu_l(E) + \nu)} W_{\nu,\, l+1/2}\left(\frac{2r}{\nu}\right) W_{\nu,\, l+}\left(\frac{2r'}{\nu}\right)\Big],$$

where $\mu_l(E)$ is the quantum defect, interpolated from the actual spectrum of the atom:

$$E_{nl} = -{}^1\!/_2 [n - \mu_l(E_{nl})]^{-2},$$

where $M_{\nu,\, l+\frac{1}{2}}$ is the Whittaker function.

Now for simplicity we shall consider the case of ionization of the electron from an s-state. For completely polarized radiation

$$\epsilon\mathbf{r} = r\sqrt{4/_3\pi}\, Y_{1m}(\mathbf{r}), \tag{9}$$

where m = 0 corresponds to linear polarization (along the z axis) and m = +1 (−1) corresponds to right-hand (left-hand) circular polarization. Having substituted expressions (2) and (9) into the expression for $K_{fi}^{(N)}(\omega)$, one can perform the integration over the angular variables. Substituting the result into (1) and then integrating over the angles of the outgoing electron, we obtain the following formulas:

a) for linearly-polarized light

$$w_n^{(N;\, l)}(\omega) = 2\pi\left(\omega\frac{F}{F_0}\right)^N \sum_{Ll_1\ldots l_{N-2} l_1'\ldots l_{N-2}'} \frac{1}{2L+1} (C^{L0}_{l_{N-2}010}\, C^{l_{N-2}0}_{l_{N-3}010} \cdots C^{l_10}_{1010})^2$$
$$\times (C^{L0}_{l'_{N-2}010}\, C^{l'_{N-2}0}_{l'_{N-3}010} \cdots C^{l_1'0}_{1010})^2\, T_{Ll_{N-2}\ldots l_1} T^*_{Ll'_{N-2}\ldots l_1'}; \tag{10}$$

b) for circularly-polarized light

$$w_n^{(N;\, c)}(\omega) = 2\pi\left(\omega\frac{F}{F_0}\right)^N \frac{N!}{(2N+1)!!}\,|T_{NN-1\ldots 2}|^2, \tag{11}$$

where

$$T_{Ll_{N-2}\ldots l_1} = \langle R_L|\, r_N g_{l_{N-2}}(E_i + (N-1)\omega;\, r_N, r_{N-1}) \ldots$$
$$\ldots g_{l_1}(E_i + 2\omega;\, r_3, r_2)\, r_2 g_1(E_i + \omega;\, r_2, r_1)\, r_1\, |n\rangle. \tag{12}$$

Only one matrix element T, corresponding to a step-by-step increase of the orbital angular momentum of the electron by unity associated with the absorption of each quantum, appears in formula (11). One can easily understand this if it is taken into consideration that during the absorption of each circularly-polarized photon the magnetic quantum number of the electron must change by +1 for right-hand polarized light and by −1 for left-hand polarized light.

In what follows it is convenient to represent w in the form

$$w_n^{(N)}(\omega) = B_n^{(N)}\eta_n^{(N)}(\omega),$$
$$B_n^{(N)} = \frac{\alpha c}{a}\frac{1}{8\pi^2}\left(\frac{F}{F_0}\right)^N\frac{2^N}{I_n^{N-2}}\left[\frac{(n+N)!}{n!}\right]^4, \qquad (13)$$

where the factor B determines the order of magnitude of the ionization probability, and the quantity η depends on the structure of the excited states of the atom, and I_n denotes the ionization potential of the n-th level in atomic units. The possibility of separating out the factor B from the general expression for w is based on a rough estimate of the matrix elements $K_{fi}^{(N)}(\omega)$.

3. THREE-PHOTON IONIZATION OF HYDROGEN AND HELIUM

Now let us apply the formulas derived above in order to calculate the three-photon ionization of hydrogen and helium. In the case of the absorption of three photons, expressions (10) and (11) take the form

$$w_n^{(l)} = 2\pi\left(\frac{\omega F}{F_0}\right)^3\left\{\frac{1}{27}\left[T_{10}+\frac{4}{5}T_{12}\right]^2+\frac{4}{175}T_{32}^2\right\},$$
$$w_n^{(c)} = 2\pi\left(\frac{\omega F}{F_0}\right)^3\frac{2}{35}T_{32}^2.$$

1. Hydrogen. For the pure Coulomb potential ($\delta_l = 0$, $\mu_l = 0$) $g_l(E; r, r')$ goes over into the exact Green's function for the hydrogen atom. Using this Green's function one can obtain an analytic expression for the cross section for three-photon ionization, in the same way that this is done in article [11] in the case of two-photon ionization. However, the obtained expressions turn out to be rather cumbersome and inconvenient for numerical analysis. Therefore we use an algorithm, common for all atoms, for calculating the matrix elements of T on an electronic computer, where the details of this algorithm are described in [14].

The curves of η as a function of ω for the ground state of hydrogen are shown in Fig. 1; here $B_{1S} = 0.833 \times 10^{-82}\,F^3\,sec^{-1}$. Our results are in satisfactory agreement with the results[5] in the range of frequencies up to the first resonance; however, at larger frequencies the results differ by a factor of several times.

The cross section for three-photon ionization of the metastable 2s-state of hydrogen is shown in Fig. 2; $B_{2S} = 1.30 \times 10^{-80}\,F^3\,sec^{-1}$. It is interesting to note that the 2s-state of hydrogen can be ionized by two quanta of a ruby laser ($\omega = 14402.2\ cm^{-1}$) or by three quanta of a neodymium laser ($\omega = 9433\ cm^{-1}$). The cross sections of these processes turn out to be equal when the flux $F \approx 10^{31}\ cm^{-2}\,sec^{-1}$.

2. Helium. The wave functions $|i\rangle$ and $|f\rangle$, constructed according to the quantum defect method, were used to calculate η for the ionization of He. In the calculation of the wave function $R_l(k; r)$ of the continuous spectrum according to formula (6), the nonregular function $G_l(k; r)$ was multiplied by the cutoff factor $(1 - e^{-10r/l(l+1)})^{2l+1}$, this choice being proposed by Seaton[15] in order to obtain the best agreement of the QDM wave functions with the Hartree-Fock orbitals. The phases δ_l of the final state wave functions were calculated according to the well-known formula $\delta_l(E) = \pi\mu_l(E)$ (see [15]), where $\mu_l(E)$ is the quantum defect, extrapolated into the region $E > 0$ according to the actual spectrum of the helium atom.[16] A graph showing the dependence $\eta(\omega)$ for the triplet metastable state of He is shown on Fig. 3; $B_{2^3S_1} = 0.927 \times 10^{-80}\,F^3\,sec^{-1}$. The dependence $\eta(\omega)$ for the singlet metastable state of He is shown on Fig. 4; $B_{2^1S_0} = 1.11 \times 10^{-80}\,F^3\,sec^{-1}$. As already mentioned, for circularly-polarized light the probability of ionization is determined by the single matrix element T_{32}, which does not contain the pole terms corresponding to intermediate two-photon resonances in the s-states, which is clear from the behavior of the curves $\eta^{(c)}(\omega)$ shown in Figs. 3 and 4.

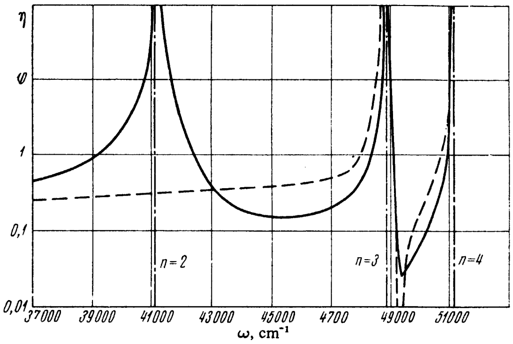

FIG. 1. The dimensionless parameter η determining the probability for three-photon ionization of the ground state of hydrogen (see Eq. (13)). The solid curve is for the case of linearly-polarized light, and the dashed curve is for the case of circularly-polarized light. The dot-dashed lines indicate the positions of the two-photon resonances.

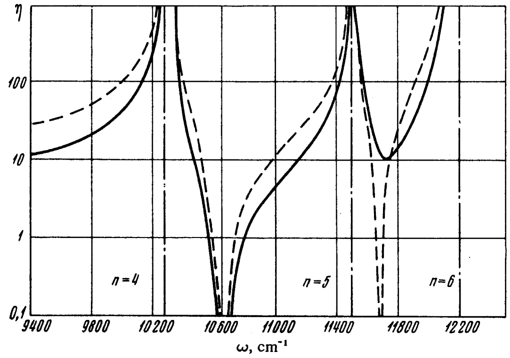

FIG. 2. Three-photon ionization of the 2s-level of hydrogen. The notation is the same as in Fig. 1.

In the case of the hydrogen atom, the spectrum of the s-states coincides with the spectrum of the d-states; therefore the resonances $\eta^{(c)}$ and $\eta^{(l)}$ also coincide, with the exception of the resonance associated with n = 2 for the ionization of the ground state of hydrogen (see Fig. 1).

It is not difficult to verify that in each interval between the poles, the matrix element T_{32} has different signs at the ends of the interval; therefore a point ω_0 exists inside the interval, at which $T_{32}(\omega_0) = 0$. Thus, for circularly-polarized light there are frequencies for which $w^{(c)}(\omega) = 0$. However, in the case of linearly-

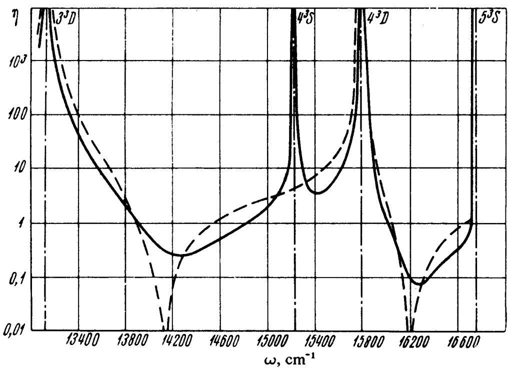

FIG. 3. Three-photon ionization of the 2^3S_1-level of helium. The notation is the same as in Fig. 1.

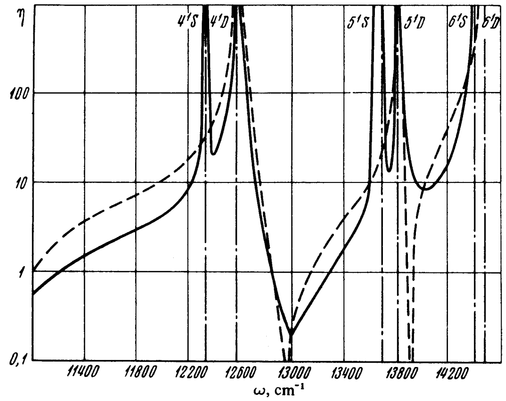

FIG. 4. Three-photon ionization of the 2^1S_0-level of helium. The notation is the same as in Fig. 1.

polarized light the probability is represented by the sum of the squares of two terms, which vanish at different frequencies; therefore $w^{(l)}$ does not vanish.

At the frequency of a ruby laser

$$w^{(l)}_{2^3S_1} = 3.09\cdot 10^{-81} F^3 \text{ sec}^{-1},\ w^{(l)}_{2^1S_0} = 3.30\cdot 10^{-78} F^3 \text{ sec}^{-1}.$$

The increase of $w^{(l)}_{2^1S_0}$ by three orders of magnitude in comparison with $w^{(l)}_{2^3S_1}$ is associated with the fact that the energy of two quanta from a ruby laser is close to the $6^1S_0-2^1S_0$ transition energy in the He atom (the frequency difference is $\lesssim 30$ cm^{-1}). For the reduction of this difference it is necessary to take into account the shift and broadening of the 2^1S_0 and 6^1S_0 levels in the presence of the field.

The shift of the 2^1S_0 level has been calculated by the method described in [14]: $\alpha_{2^1S_0} = 270$ atomic units. The shift and broadening of the 6^1S_0 level are determined by the real and imaginary parts of the polarizability $\alpha_{6^1S_0}$:

$$\operatorname{Re}(\Delta E) = -{}^1\!/_4\mathscr{E}^2 \operatorname{Re}\alpha, \quad \operatorname{Im}(\Delta E) = -{}^1\!/_4\mathscr{E}^2 \operatorname{Im}\alpha.$$

The value of Re $\alpha_{6^1S_0}$ was calculated according to formulas (7) and (4), and the Im $\alpha_{6^1S_0}$ is expressed in terms of the cross section for one-photon ionization, given by Eq. (8). For the frequency corresponding to a ruby laser

$$\operatorname{Re}\alpha_{6^1S_0} = 300 \text{ a.u.},\quad \operatorname{Im}\alpha_{6^1S_0} = 35 \text{ a.u.}$$

Therefore, for field intensities $\lesssim 10^6$ V/cm the shift and broadening of the levels cannot substantially change the probability for the process.

The experimental value of the upper limit for the probability of three-photon ionization of metastable helium for a field intensity $\mathscr{E} = 2 \times 10^5$ V/cm, which was obtained in article [17], is equal to 4.7×10^{-71} F^3 sec^{-1}. In this work the total flux of ions produced by ionization of singlet and triplet atoms was measured. In order to make a quantitative comparison of theory with experiment, further experimental investigation of the three-photon ionization of metastable helium is of interest.

In conclusion we note that a calculation of the four-photon ionization of the ground state of the potassium atom has been carried out by the method proposed by one of the authors of the present article. The results of the calculation together with the experimental findings are discussed in detail in article [18]; here we only note that the theoretical value for the probability of the process is within the limits of the experimental error.

The authors thank I. Bakos, G. A. Delone, and N. B. Delone for helpful discussions.

---

[1] N. B. Delone and L. V. Keldysh, Preprint No. 11, FIAN, 1970.

[2] N. B. Delone and G. A. Delone, Zh. Eksp. Teor. Fiz. 54, 1067 (1968) [Sov. Phys.-JETP 27, 570 (1968)].

[3] G. Baravian, R. Benattar, J. Bretagne, J. L. Godart, and G. Sultan, Appl. Phys. Letters 16, 162 (1970).

[4] Wolfgang Zernik, Phys. Rev. 135, A51 (1964).

[5] Y. Gontier and M. Trahin, Phys. Rev. 172, 83 (1968).

[6] Charles Schwartz and J. J. Tiemann, Ann. Phys. (N.Y.) 6, 178 (1959).

[7] Wolfgang Zernik, Phys. Rev. 176, 420 (1968); F. T. Chan and C. L. Tang, Phys. Rev. 185, 42 (1969).

[8] H. Barry Bebb and Albert Gold, Phys. Rev. 143, 1 (1966).

[9] V. M. Morton, Proc. Phys. Soc. (London) 92, 301 (1967).

[10] H. Barry Bebb, Phys. Rev. 149, 25 (1966); 153, 23 (1967).

[11] L. P. Rapoport, B. A. Zon, and N. L. Manakov, Zh. Eksp. Teor. Fiz. 56, 400 (1969) [Sov. Phys.-JETP 29, 220 (1969)].

[12] B. A. Zon, N. L. Manakov, and L. P. Rapoport, Dokl. Akad. Nauk SSSR 188, 560 (1969) [Sov. Phys.-Doklady 14, 904 (1970)].

[13] L. Curtiss, Coulomb Wave Functions, (Russ. transl.) VTs Akad. Nauk SSSR, 1969.

[14] V. A. Davydkin, B. A. Zon, N. L. Manakov, and L. P. Rapoport, Zh. Eksp. Teor. Fiz. 60, 124 (1971) [Sov. Phys.-JETP 33, 70 (1971)].

[15] M. Seaton, Monthly Not. Roy. Astr. Soc. 118, 117 (1958); A. Burgess and M. Seaton, Monthly Not. Roy. Astr. Soc. 120, 191 (1960).

[16] Atomic Energy Levels, edited by C. E. Moore, Nat. Bur. Std. (U.S.) Circ. No. 467 (U.S. Government Printing Office, Washington, D. C., 1949).

[17] I. Bakos, I. Kantor, and A. Kish, ZhETF Pis. Red. **12**, 371 (1970) [JETP Lett. **12**, 255 (1970)].

[18] G. A. Delone, N. B. Delone, N. L. Manakov, and G. A. Piskova, Zh. Eksp. Teor. Fiz., in press.

Translated by H. H. Nickle
98