CALCULATION OF THE SPECTRA OF POTASSIUM-LIKE MULTICHARGED IONS

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The energy levels and oscillator strengths for dipole transitions between the levels of low-lying configurations are calculated for ions of the KI isoelectronic sequence. The calculations are based on the energy approach to the effective potential method with the most important polarization effects taken into account, including core polarization by the outer electron. The results, some of which are obtained here for the first time for potassium-like ions, can be useful in a number of related fields, such as laser physics, plasmas, and so on.

INTRODUCTION

We consider the spectroscopic characteristics (energy levels and transition oscillator strengths) of multicharged ions of the isoelectronic sequence KI. This problem is important because of a number of factors. Spectroscopic information on multicharged ions, particularly potassium-like ions, plays an important role in numerous applications, including the creation of ion sources, the operation of shortwave lasers on multicharged ions, plasma diagnostics, and so on [1-4]. The experimental and theoretical study of multicharged ions is complicated because correlation and relativistic effects must be taken into account simultaneously. For many multicharged ions, such as highly-charged potassium-like ions, spectroscopic information either does not exist or is limited, extremely fragmented, and is available mainly for the first terms of the isoelectronic series [4]. This is especially true for potassium-like ions. Data on the energy levels and oscillator strengths exist for the first terms of the series: KI, CaII, ScIII, TiIV, VV. For the first two ions the information is fairly detailed and oscillator strengths are known for the transitions $n\ell$—$n'\ell'$ with $n,n' = 4$-10, ℓ, $\ell' = 0$-4. But for the other ions information is scarce and is available only for certain particular transitions (see [5-13]). The most complete study of the energy spectra of potassium-like ions is apparently [13], while [12] is the most complete study of the oscillator strengths. The calculations of [12] use the approximation of a nonrelativistic screened Coulomb potential. Below we consider potassium-like ions with nuclear charges $Z = 23$-28. Oscillator strengths of the following dipole transitions are calculated:

$$4s^2S_{\frac{1}{2}} - 4p^2P_{\frac{1}{2}\frac{3}{2}}, \ 5s^2S_{\frac{1}{2}} - 4p, \ 5p^2P_{\frac{1}{2}\frac{3}{2}}, \ 6s^2S_{\frac{1}{2}} - 5p, \ 6p^2P_{\frac{1}{2}\frac{3}{2}},$$

$$4p^2P_{\frac{1}{2}\frac{3}{2}} - 3d^2D_{\frac{3}{2}\frac{5}{2}}, \ 6p^2P_{\frac{1}{2}\frac{3}{2}} - 5d^2D_{\frac{3}{2}\frac{5}{2}}.$$

We use the S-matrix formalism (energy approach) [14-20]. This is a well-known procedure in atomic theory for calculating energy shifts of degenerate states [14]. It is based on the diagonalization of a secular matrix constructed using the adiabatic formula of Gell-Mann and Low. A similar approach using this formula and the electrodynamic scattering matrix has been developed for the relativistic atom [16, 17]. The matrix elements of the secular operator in the relativistic approximation for the excited states are complex to second order in relativistic perturbation theory. The imaginary part is related to the probability of radiative decay. The energy approach was formulated in [16] for one and two-electron atoms and was used to calculate their total radiative and self-ionization widths. The same approach was extended in [18] to the relativistic calculation of the probabilities of radiative and Auger decay of excited states in many-electron atoms. The problem of taking into account the most important polarization effects to the radiative decay of excited states, in particular core polarization by the outer (valence) electrons, was solved systematically using quantum electrodynamics for the first time in [20]. Numerous calculations of oscillator strengths show that to obtain an accuracy equal to that of the latest experimental measurements it is neces-

sary to take into account the effects of core polarization, at least for transitions between the levels of low-lying configurations [20-24]. The effect of core polarization was studied in [22-24] for alkali atoms (Li, Na, K, Cs). It was shown numerically that the correction to the oscillator strengths due to polarization increases from 1% to 16% as we progress from Li to Cs. For ions of the KI isoelectronic sequence core polarization can become very significant (up to 10%), as shown by calculations of oscillator strengths for dipole transitions between levels of low-lying configurations of ions with Z = 23-28. We next discuss certain details of the method of calculation.

2. METHOD OF CALCULATION

We consider radiative decay of an excited state of an ion with one outer electron above a core of filled electron shells. Potassium-like ions are an example of this type of atomic system. The ground configuration of a potassium-like ion is

$$1s^2 2s^2 2p^6 3s^2 3p^6 4s.$$

To second order in electrodynamic perturbation theory the decay is described by a Feynman diagram of the form $A = \underline{}\int$. Calculating this diagram using the adiabatic formula of Gell-Mann and Low with the relativistic scattering matrix, we obtain the following expression for the imaginary part of the electronic energy of the atom (which is related to the decay probability) [18]:

$$\mathrm{Im}\,\Delta E\,(A) = -\frac{1}{4\pi} \sum_{\substack{a>n>\gamma \\ a\leqslant n\leqslant\gamma}} V^{|\omega_{an}|}_{anan}, \tag{1}$$

where $\sum\limits_{a>n>\gamma}$ refers to electrons, $\sum\limits_{a\leqslant n\leqslant\gamma}$ refers to vacancies (in the core), and the matrix elements $V^{|\omega|}$ have the form

$$V_{ij\kappa l} = <ij\,|\,\frac{\sin|\omega|r_{12}}{r_{12}}\,(1-\alpha_1\alpha_2)\,|\kappa l>. \tag{2}$$

Here and below we use atomic units $e = \hbar = m = 1$ for convenience; α_1, α_2 are Dirac matrices and ω is the transition frequency. The individual terms in the sum over n in (1) correspond to the partial contributions of the different decay channels. Hence the probability of the transition $\alpha\text{--}n$ is, in this approximation

$$\Gamma_{\alpha n} = \frac{1}{4\pi}\,V^{|\omega_{an}|}_{anan}, \tag{3}$$

and the oscillator strength gf is defined as

$$gf = \lambda^2 g'\Gamma_{\alpha n}/6{,}67\cdot10^{15}, \tag{4}$$

where g and g' are the degrees of degeneracy and λ is the wavelength of the transition expressed in angstroms. The matrix element (2) is calculated using the wave functions of the outer electron. They are the eigenfunctions of the one-particle Dirac equation

$$\left[-iac\nabla + \beta c^2 - \frac{Z}{r} + V_M(r)\right]\varphi_{nlj} = \varepsilon_{nlj}\,\varphi_{nlj} \tag{5}$$

with an effective potential $V_M(r)$ describing the interaction between the outer electron and the $1s^2 2s^2 2p^6 3s^2 3p^6$ core. We use the Ivanov–Ivanova effective potential, which has been used successfully in various atomic problems. It is given by [25]

$$V_M(r\,|\,b) = \left\{2\,[1 - e^{-2r}\,(1+r)] + (N-2)\times\right.$$
$$\left.\times\left[1 - e^{-br}\left(1 + \frac{3}{4}\,br + \frac{1}{4}\,b^2r^2 + \frac{1}{16}\,b^3r^3\right)\right]\right\}. \tag{6}$$

TABLE 1. Energy Levels of Potassium-like Ions (in 100 cm^{-1}) Calculated in the Present Paper

Transition		ScIII	TiIV	VV	CrVI	MnVII	FeVIII
$4s^2S_{1/2}$		1741	2686	3784	5033	6433	7981
	*	1741	2686	3784	5032	6433	—
$4p^2P_{1/2}$		1376	2211	3201	4346	5643	7082
	*	1376	2211	3201	4345	5643	7081
$4p^2P_{3/2}$		1371	2202	3189	4328	5619	7030
	*	1371	2202	3189	4327	5619	7028
$4d^2D_{3/2}$		874	1522	2326	3277	4361	5566
$4d^2D_{5/2}$		873	1521	2325	3275	4358	5562
$5s^2S_{1/2}$		848	1366	1983	2692	3481	4342
$5p^2P_{1/2}$		716	1184	1750	2419	3191	4075
$5p^2P_{3/2}$		714	1180	1745	2411	3179	4059

*Experimental data.

TABLE 2. Oscillator Strengths of Dipole Transitions in Potassium-like Ions

Transition	VV [12]	VV	CrVI	MnVII	FeVIII	CoIX	NiX
$4s^2S_{\frac{1}{2}} - 4p^2P_{\frac{1}{2}\frac{3}{2}}$	0,899	0,91	0,87	0,83	0,79	0,76	0,72
$5s^2S_{\frac{1}{2}} - 4p^2P_{\frac{1}{2}\frac{3}{2}}$	0,132	0,14	0,13	0,12	0,11	0,10	0,08
$5s^2S_{\frac{1}{2}} - 5p^2P_{\frac{1}{2}\frac{3}{2}}$	1,279	1,29	1,16	1,06	0,94	0,82	0,69
$6s^2S_{\frac{1}{2}} - 5p^2P_{\frac{1}{2}\frac{3}{2}}$	0,229	0,22	0,20	0,18	0,16	0,15	0,13
$6s^2S_{\frac{1}{2}} - 6p^2P_{\frac{1}{2}\frac{3}{2}}$	1,621	1,62	1,48	1,34	1,22	1,12	0,98
$4p^2P_{\frac{1}{2}\frac{3}{2}} - 3d^2D_{\frac{3}{2}\frac{5}{2}}$	0,051	0,048	0,042	0,039	0,036	0,033	0,028
$6p^2P_{\frac{1}{2}\frac{3}{2}} - 5d^2D_{\frac{3}{2}\frac{5}{2}}$	0,40	0,41	0,38	0,36	0,35	0,31	0,27

Here N = 18 is the number of core electrons and b is a parameter which, as usual in the study of isoelectronic sequences, is written in the form $b(Z) = \sum_{\kappa} b_\kappa Z^{-\kappa}$, where the b_κ are empirical constants. These constants were determined using experimental and compiled values of the energy levels of the ions SIII, TiIV, VV, FeVIII [7-9, 13]. In the first step of the calculation the Dirac equation for given $\varepsilon_{n\ell j}$ was considered as an equation for the eigenvalues of the parameter b (the Sturm problem). The parameter b is chosen such that

$$R_1(r) \to 0, \quad R_2(r) \to 0, \quad R \to \infty,$$

where R_1 and R_2 are the large and small components of the Dirac wave function. They satisfy the following equations obtained from (5):

$$\tilde{R}'_1 = -\frac{|\varkappa| + \varkappa}{r} \tilde{R}_1 + \tilde{\alpha} Z \left[\varepsilon + 2(\tilde{\alpha}Z)^{-2} + V_M \right] \tilde{R}_2,$$

$$\tilde{R}'_2 = \frac{|\varkappa| - \varkappa}{r} \tilde{R}_2 - \tilde{\alpha} Z \left[\varepsilon + V_M \right] \tilde{R}_1,$$

where $\quad R_1 = \tilde{R}_1 r^{|\varkappa|-1}, \quad R_2 = \tilde{R}_2 r^{|\varkappa|-1}, \quad \tilde{\alpha} = \frac{1}{c}$ (atomic units)

To use the angular symmetry of the atomic problem the potential $\sin|\omega| r_{12}/r_{12}$ in (2) is expanded in spherical harmonics. We then obtain for $V^{|\omega|}$

$$V_{1243}^{|\omega|} = [(2j_1+1)(2j_2+1)(2j_4+1)(2j_3+1)]^{1/2}(-1)^{j_1+j_2+j_3+j_4+m_1+m_2} \times$$

$$\times \sum_{\mu\nu}(-1)^{\mu}\begin{pmatrix} j_1 & j_3 & \nu \\ m_1 & -m_3 & \mu \end{pmatrix}\begin{pmatrix} j_2 & j_4 & \nu \\ m_2 & -m_4 & \mu \end{pmatrix} \operatorname{Im} Q_{\nu}(1243), \quad Q_{\nu} = Q_{\nu}^{\text{coul}} + Q_{\nu}^{\text{br}}, \tag{7}$$

where j_i and m_i are the total one-electron angular momentum and its projection, Q_{ν}^{coul} and Q_{ν}^{br} are the Coulomb and Breit parts of the matrix element corresponding to the terms $\dfrac{\sin|\omega|r_{12}}{r_{12}}$,

$\dfrac{\sin|\omega|r_{12}}{r_{12}}\alpha_1\alpha_2; \begin{pmatrix} j_1 & j_3 & \nu \\ m_1 & -m_3 & \mu \end{pmatrix}$ is the 3j symbol. The quantity Q_{ν} is determined through the radial integrals P_{ν} and the angular coefficients S_{ν}. In particular, we have for Q_{ν}^{coul}

$$Q_{\nu}^{\text{coul}} = [P_{\nu}(1243)S_{\nu}(1243) + P_{\nu}(\widetilde{1243})S_{\nu}(\widetilde{1243}) +$$

$$+ P_{\nu}(\widetilde{1243})S_{\nu}(\widetilde{1243}) + P_{\nu}(\widetilde{1243})S_{\nu}(\widetilde{1243})], \tag{8}$$

$$S_{\nu}(1243) = \{\nu l_1 l_3\}\{\nu l_2 l_4\}\begin{pmatrix} j_1 & j_3 & \nu \\ 1/2 & -1/2 & 0 \end{pmatrix}\begin{pmatrix} j_2 & j_4 & \nu \\ 1/2 & -1/2 & 0 \end{pmatrix},$$

where i denotes the large component and $\tilde{i}$ the small component ($i = 1$-4) and l_i is the orbital angular momentum. The Breit part Q_{ν}^{br} is determined in the same way. The symbol $\{\nu l_1 l_3\}$ means that $(\nu+l_1+l_3)$ is an even number; the form of P_{ν} and the detailed procedures of the numerical calculation are given in [19]. The equations given above describe the decay of an excited atomic state of a system with one outer electron above the core to lowest (second) order in perturbation theory. The corresponding diagram is $A = \underline{}\!\!\slash\!\!\underline{}$. Core polarization leads to a modification of the diagram: A: $A \to A' = \underline{}\!\!\slash\!\!\underline{}$. According to the quantum-electrodynamic procedure [20], this corresponds to the addition of the polarization interaction operator V_{pol} to the electron-electron Coulomb interaction operator in (2). The operator V_{pol} describes the interaction between the outer electron and the electrodynamic vacuum through the polarizability of the core. In the energy approach the polarization potential is equivalent to the polarization interaction between two outer particles above a core of filled electron shells through the polarizability of the core. Using the Thomas—Fermi approximation to calculate the polarization diagrams of second-order perturbation theory given the following expression for V_{pol} [26]:

$$V_{\text{pol}}(r_1, r_2) = X\{\int dr \rho_c^{1/3}(r)/|r_1 - r|\cdot|r - r_2| -$$

$$- [\int dr \rho_c^{1/3}(r)/|r_1 - r|\int dr \rho_c^{1/3}(r)/|r - r_2|]/\int dr \rho_c^{1/3}(r)\}, \tag{9}$$

where X is a numerical factor and ρ_c is the electron density of the core. We note that the angular parts of the matrix elements of the electron—electron Coulomb and polarization interaction operators are the same and hence core polarization results in a redefinition of the radial integrals of the radial parts of the matrix elements of the Coulomb interaction operator. The detailed procedure of the numerical calculation of the matrix elements of the potential (9) is discussed in [26]. As in the case of (2), the calculation reduces to solving a system of ordinary differential equations using the Runge—Kutta integration method. Use of this procedure radically simplifies the calculations and can be used successfully in various atomic problems where it is required to evaluate Coulomb integrals (for more detail see [18-20]). We also note that the equations given above for the transition probabilities and oscillator strengths correspond to the usual equations for these quantities in the form of "lengths". The S-matrix method has a number of advantages over the usual method of calculating these quantities. In particular, the S-matrix method provides a unified approach for the study and calculation of a large number of characteristics and phenomena in atomic physics (self-ionization (Auger) decay, dielectric recombination, and so on [16-18]).

3. CALCULATED RESULTS

The calculated energies $\varepsilon_{n\ell j}$ and gf factors of dipole transitions between levels of low-lying configurations in ions of the KI isoelectronic sequence are given in Tables 1 and 2. The parameter of the potential (6) was determined using information on the energy levels (compiled values) or the ions ScIII, TiIV, VV, and FeVIII [7-9, 13]. For comparison, Table 2 also gives

the oscillator strengths for the ion VV calculated using the approximation of a screened Coulomb potential [12]. Apparently these are the only calculated results available at the present time for these ions. We see that the oscillator strengths for VV obtained here closely agree with the results of the semiempirical calculation [12]. The results for the ions MnVII, FeVIII, CoIX, and NiX are evidently obtained here for the first time. Unfortunately, the quality of the calculated values cannot be accurately determined because of the lack of experimental oscillator strengths for these ions. However, the effectiveness and sufficiently high accuracy of the calculations are demonstrated convincingly by numerous applications of this method to the calculation of spectroscopic characteristics (including oscillator strengths) for a large number of multicharged ions (see [20, 29], where oscillator strengths were calculated for dipole transitions in ions of the isoelectronic sequence series NaI, AlI, GaI). For potassium-like and aluminum-like ions one expects anomalies in the behavior of gf near the neutral end of the series (see [28]) and for highly-charged terms of an isoelectronic series there can be complexities in the interpretation of experimental values and in the comparison between the experimental and calculated values (for more detail, see [27], where these anomalies are analyzed for ions of the NaI isolectronic series). Our results indicate that the behavior of the oscillator strengths for the transitions of potassium-like ions is very complicated and nonmonotonic for a number of transitions such as $4s^2S-5p$, $6p^2P$; $4p^2P-4d$, $5d^2D$; $4d^2D-4f$, $5f^2F$; here anomalous behavior is typical. A correct calculation of the oscillator strengths for these transitions requires very accurate calculations using the many-electron approximation [27-29]. The calculations show that inclusion of core polarization by the outer electron leads to a decrease in gf. This decrease is most significant (of order 10%) for 4-4 transitions, whereas for most of the 4-5 and 5-6 transitions the values of gf calculated using (2) and (2) plus (9) differ only slightly, since the matrix element of (9) calculated with the appropriate wave functions is small. Finally we note that quite accurate values for the oscillator strengths can be obtained using ideal potentials in most cases, especially for atomic systems with one outer electron above a core of closed electron shells. However, care must be exercised in analyzing the results based on the one-electron approximation of the effective potential if gf exhibits anomalous behavior for any of the ions of the series (for example, for aluminum-like ions near the neutral end of the series, highly-charged sodium-like ions, and so on [27-29]). The results obtained here are applicable from this point of view and can be used in various applications such as plasma diagnostics, laser physics, astrophysics, and so on.

LITERATURE CITED

1. L. A. Vainshtein and V. P. Shevel'ko, Structure and Characteristics of Ions in a Hot Plasma [in Russian], Nauka, Moscow (1986).
2. P. G. Burke, W. B. Eisner, D. G. Hammer, et al., Atoms in Astrophysics [Russian translation], Mir, Moscow (1986).
3. A. V. Glushkov and E. P. Ivanova, Spectroscopy of Multicharged Ions [in Russian], Nauka, Moscow (1986), pp. 5-65.
4. É. Ya. Kononov and A. N. Ryabtsev, Izv. Akad. Nauk SSSR, Ser. Fiz., 46, No. 4, 641-645 (1984).
5. C. E. Magnusson and P. O. Zetterberg, Phys. Scripta, 10, No. 1, 177-181 (1977).
6. G. Risberg, Ark. Fys. (Stockholm), 37, No. 2, 231-235 (1968).
7. C. H. Van Deurzen, T. G. Conway, and S. P. Davis, J. Opt. Soc. Am., 63, No. 1, 158-162 (1973).
8. J. W. Swensson and G. B. Edlen, Phys. Scripta, 63, No. 1, 158-162 (1974).
9. J. O. Ekberg, Phys. Scripta, 9, No. 1, 96-99 (1974).
10. J. O. Ekberg, Phys. Scripta, 8, No. 1, 35-40 (1973).
11. C. E. Moore, Atomic Energy Levels NBS, 35 (1971).
12. A. Lingard and S. E. Nielssen, At. Data Nucl. Data Tables, 19, No. 6, 533-635 (1977).
13. S. V. Malinovskaya, Opt. Spektrosk., 64, No. 2, 441-443 (1988).
14. V. V. Tolmachev, Adv. Chem. Phys., 14, No. 2, 421-489 (1969).
15. L. N. Ivanov, E. P. Ivanova, and V. V. Tolmachev, Izv. Vyssh. Uchebn. Zaved., Fiz., No. 12, 84-89 (1969).
16. Yu. Yu. Dmitriev and L. N. Labzovskii, Theory of Atoms and Atomic Spectroscopy [in Russian], Latvian State University, Riga (1973), pp. 93-98.

17. L. N. Labzovskii, Zh. Éksp. Teor. Fiz., 59, No. 2, 169-174 (1970).
18. L. N. Ivanov, Doctoral Dissertation, Moscow (1985).
19. L. N. Ivanov and V. S. Letochov, Comm. Mod. Phys., D 12, No. 4, 169-192 (1985).
20. A. V. Glushkov, L. N. Ivanov, and E. P. Ivanova, Self-Ionization Phenomena in Atoms [in Russian], Moscow State Univ., Moscow (1986), pp. 58-86.
21. W. A. Goddard III, Phys. Rev., 182, No. 1, 48-54 (1969).
22. A. Hibbert, Adv. At. Mol. Phys., 18, No. 2, 309-340 (1982).
23. J. C. Weisheit and A. Dalgarno, Chem. Phys. Lett., 9, No. 4, 517-520 (1971).
24. J. Migdalec and W. E. Baylis, J. Phys., B 12, No. 10, 1113-1119 (1979).
25. L. N. Ivanov and E. P. Ivanova, At. Data Nucl. Data Tables, 23, No. 2, 95-109 (1979).
26. E. P. Ivanova, L. N. Ivanov, A. E. Kramida, and A. V. Glushkov, Phys. Scripta, 32, No. 4, 513-524 (1985).
27. R. J. S. Grossley, L. J. Curtis, and C. F. Fischer, Phys. Lett., A 57, No. 3, 220-222 (1976).
28. K. H. Huang, Argonne National Lab Report, 1983.
29. A. V. Glushkov, Many-Particle Effects in Atoms [in Russian], Nauka, Moscow (1985), pp. 103-116.

MAGNETOOPTIC ACTIVITY AND SYMMETRY OF PETROLEUM VANADYL PORPHYRINS

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We report magnetooptic rotation and magnetic circular dichroism spectra in the vicinity of the absorption bands at 17410 cm^{-1} and 16760 cm^{-1} in chloroform solutions of petroleum vanadyl porphyrin. Using the moment method, we estimate the original splitting and the z-component of the magnetic moment of the 1^1E_{1u} level for both synthetic and petroleum vanadyl porphyrins. We conclude that petroleum vanadyl porphyrins exhibit D_{2h} symmetry.

The goal of the present work is to study magnetic circular dichroism (MCD) spectra and the magnetic circular birefringence (MCB) of synthetic and petroleum vanadyl porphyrins and to use them to analyze the symmetry of these porphyrin molecules.

The general term "porphyrin" is used (see [1-4], and references cited therein) to describe porphin derivatives which differ from it by the presence of various substituents at one position or another on the porphin ring. The most important property of porphyrins is their ability to form stable complexes with metals, so-called metalloporphyrins. The presence of a metal occupying a position on the axis of the porphyrin ring leads to an increase in the symmetry of the molecule from D_{2h} to D_{4h}, if the metal ion is located in the plane of the ring, or to C_{4v} if it is located outside that plane [1].

The visible spectrum of metalloporphyrins consists of two bands, with intensities and positions which depend on the type of metal involved. The longer wavelength absorption band is attributed to the pure electronic Q(0-0) transition between the 1^1A_{1g} ground state and the doubly degenerate 1^1E_{1u} states in the D_{4h} group of the porphyrin ring. In [4] it was shown that in a number of metalloporphyrins, the side substituents, axial ligands, and solvent molecules may lower the symmetry of the porphyrin ring, thus lifting the degeneracy of the 1^1E_{1u} level, and splitting the Q(0-0) band. The size of this splitting is less than the width Γ of the Q(0-0) band and is observable only when the MCD, MCB, and absorption spectra are all analyzed together. The size of the initial splitting may be estimated from the distortion of the D_{4h} symmetry of the porphyrin ring in various metalloporphyrins.