

ATOMIC SPECTROSCOPY

Effective Hamiltonian for Valence Electrons of an Atom

M. G. Kozlov and S. G. Porsev

St. Petersburg Institute of Nuclear Physics, Gatchina, Leningradskaya oblast, 188350 Russia
e-mail: mgk@mfl309.spb.edu

Received June 10, 1998

Abstract—Variants of the construction of the effective Hamiltonian for valence electrons of an atom are discussed. It is shown that a proper choice of the optimum initial approximation can substantially improve the agreement between calculated and experimental spectra of multielectron atoms. The optimized effective Hamiltonian can be used for calculations of atomic quantities.

INTRODUCTION

In [1], a method was suggested for calculating the low-energy part of the spectrum of a multielectron atom by solving the eigenvalue problem for the effective Hamiltonian H_{eff} of valence electrons. The Hamiltonian H_{eff} was constructed using the many-body perturbation theory (MPT) for the residual interaction of valence electrons with an atomic core. Such an approach resulted in the improvement of the accuracy of calculations of spectra of a number of heavy atoms containing two or three valence electrons [1–4]. The method yields the transition probabilities, constants of the hyperfine interaction, and other atomic quantities [5]. In addition, it was applied recently to calculations of the hyperfine structure and P -, T -odd interactions in BaF [6] and YbF [7] molecules.

The advantage of the method [1] over the other methods for accounting for electronic correlations (see, for example, [8]) is the possibility of constructing the effective Hamiltonian in the multidimensional space. This permits, in principle, calculations of atoms containing many valence electrons. In this paper, we consider the problem of the optimum choice of the initial MPT approximation depending on the number of valence electrons. This problem becomes especially important for systems containing more than three valence electrons. Such calculations are necessary, for example, in connection with precision experiments on parity nonconservation in lead and bismuth atoms [9, 10]. Molecular calculations also often deal with a great number of valence electrons.

The effective Hamiltonian consists of two parts:

$$H_{\text{eff}}(E) = H_{\text{FC}} + \Sigma(E), \quad (1)$$

where H_{FC} is the Hamiltonian in the frozen atomic core approximation and Σ is the energy-dependent correction, which takes into account virtual core excitations. It is assumed that the energy E is insufficient for excitation of the atomic core electrons.

By introducing the projector P to the multielectron subspace, which corresponds to the frozen atomic core, the operators H_{FC} and Σ can be written in the form

$$H_{\text{FC}} = PHP, \quad (2)$$

$$\Sigma(E) = PV R_Q(e)VP, \quad (3)$$

where H is the many-body Hamiltonian; $Q = 1 - P$, V is the operator of the residual interaction between electrons, which will be defined below; and $R_Q(E)$ is the Green function in the Q space:

$$R_Q(E) = (E - QHQ)^{-1}. \quad (4)$$

The atomic spectrum is found from the equation

$$H_{\text{eff}}(E_n)\Phi_n = E_n\Phi_n, \quad (5)$$

which is solved in the P space, but is equivalent to the full multielectron Schrödinger equation. It is obvious that the effective Hamiltonian can be constructed only within a framework of some approximation. For example, the Hartree–Fock approximation for the Green function (4) can be used, which results in good agreement between theoretical and experimental spectra for a number of heavy atoms [1–3]. In this paper, we study the energy dependence of the operator Σ in more detail and suggest the method for refining the theory, which requires no substantial complications. As an example, we refer to spectra of barium, mercury, and thallium.

ONE-PARTICLE APPROXIMATION

Consider a set of one-particle orbitals ϕ_n and the corresponding one-particle energies ϵ_n (assuming that $\epsilon_n \geq \epsilon_{n-1}$). We assume that the first N_c orbitals belong to the atomic core and introduce the state $|0\rangle$, in which only orbitals with $n \leq N_c$ are occupied. Let us introduce creation operators for particles a_i^\dagger , $i > N_c$ and holes b_n^\dagger ,

$n \leq N_c$. These operators allow one to construct many-body basis states in the P and Q subspaces:

$$P: a_{i_{N_v}}^\dagger \dots a_{i_1}^\dagger |0\rangle, \quad (6)$$

$$Q: \begin{cases} b_{n_1}^\dagger a_{i_{N_v}}^\dagger \dots a_{i_1}^\dagger |0\rangle \\ b_{n_2}^\dagger b_{n_1}^\dagger a_{i_{N_v}}^\dagger \dots a_{i_1}^\dagger |0\rangle \\ \dots \end{cases} \quad (7)$$

where N_v is the number of valence electrons.

The Hamiltonian H_{FC} can be now written in the form

$$H_{FC} = E_{\text{core}} + \sum \varepsilon_i a_i^\dagger a_i + \frac{1}{2} \sum V'_{i_1, i_3, i_1, i_2} a_{i_4}^\dagger a_{i_3}^\dagger a_{i_2} a_{i_1}, \quad (8)$$

where V'_{i_1, i_3, i_1, i_2} are matrix elements of the residual interaction and

$$E_{\text{core}} = \langle 0|H|0\rangle \quad (9)$$

is the atomic core energy.

By omitting the residual interaction V' in the Hamiltonian H , we obtain the following one-particle operator

$$H_0 = E_{\text{core}} + \sum \varepsilon_i a_i^\dagger a_i - \sum \varepsilon_n b_n^\dagger b_n. \quad (10)$$

This operator is a diagonal one in the representation (6), (7), and, hence, it does not intermix the P and Q subspaces. The quality of approximation (10) is determined by the magnitude of the residual interaction, which is equal to the difference between the exact and one-particle Hamiltonians

$$V' \equiv H - H_0. \quad (11)$$

It follows from the definition of the operator H_0 that $\langle 0|V'|0\rangle = 0$; however, the average value of the operator V' for the wave functions (6) and (7) rapidly increases with increasing N_v . This is explained by the well-known fact that the interaction between electrons is twice taken into account in a sum $\sum \varepsilon_i$ of one-particle energies. Such sums appear when the operator H_0 is used for the construction of the approximate Green function

$$\begin{aligned} R_Q^0(E) &\equiv (E - QH_0Q)^{-1} \\ &= Q(E_v - \sum \varepsilon_i a_i^\dagger a_i + \sum \varepsilon_n b_n^\dagger b_n)^{-1} Q, \end{aligned} \quad (12)$$

where $E_v = E - E_{\text{core}}$.

Let us see what happens when this expression is used instead of the exact Green function in (3). The summation is carried out over the intermediate states with one or two holes, because the residual interaction operator is two-particle. The matrix elements $R_Q^0(E)$ for the corresponding basis vectors (7) include differences of two sums of Hartree-Fock energies. Each of the sums overestimates the interelectron interaction; however, the hole sum always contains one or two

terms, whereas the number of terms in the particle sum is greater by N_v and increases with increasing N_v .

We see that the operator $R_Q^0(E)$ cannot be a good approximation to the exact Green function when N_v is large. Note that the definition of the Green function (12) corresponds to the Brillouin-Wigner MPT, which is known to be inadequate for a great number of particles (see, for example, [11], ch. 4). On the other hand, the initial Hamiltonian can be easily improved by introducing the new operator

$$H_0^\delta = H_0 + \delta. \quad (13)$$

The shift δ can be chosen, for example, in such a way that the correction to the ground-state energy Φ_G of an atom would be zero:

$$\langle \Phi_G | H - H_0^\delta | \Phi_G \rangle = 0, \Rightarrow \delta = \langle \Phi_G | V' | \Phi_G \rangle. \quad (14)$$

The replacement of the operator (10) by (13) results in the redefinition of the residual interaction operator:

$$V' \longrightarrow V'^\delta = V' - \delta. \quad (15)$$

It is obvious that such a replacement does not change the form of expression (3), which contains nondiagonal matrix elements of the residual interaction, but leads to the replacement of the one-particle Green function:

$$R_Q^0(E) \longrightarrow R_Q^0(E - \delta) = (E - \delta - QH_0Q)^{-1}. \quad (16)$$

Thus, in the lowest MPT order, when the Green function in (3) is replaced by the one-particle Green function, the use of Hamiltonian (13) instead of (10) is equivalent to the replacement $\Sigma(E) \longrightarrow \Sigma(E - \delta)$. We will use this below in the discussion of the dependence of the theoretical spectrum on the choice of δ . Note that if δ is determined from condition (14) and the function Φ_G is represented in the one-determinant approximation of the type (6), then

$$E - \delta = E - E_G + E_G^0, \quad (17)$$

where $E_G^0 = \langle \Phi_G | H_0 | \Phi_G \rangle$.

This means that when $E = E_G$ in the ground state, the Green function (16) coincides with the Green function in the Rayleigh-Schrödinger MPT, which allows one to expect a faster convergence for a great number of particles. In this case, the main advantage of the Brillouin-Wigner perturbation theory is retained—the possibility of the construction of the effective operator in the subspace of an arbitrary dimensionality without imposing the conditions of quasi-degeneracy of the levels of the Hamiltonian H_0 .

CHOICE OF THE PARAMETER δ

As was shown above, taking into account the shift δ , equation (5) has the form

$$H_{\text{eff}}(E_n - \delta)\Phi_n = E_n\Phi_n. \quad (18)$$

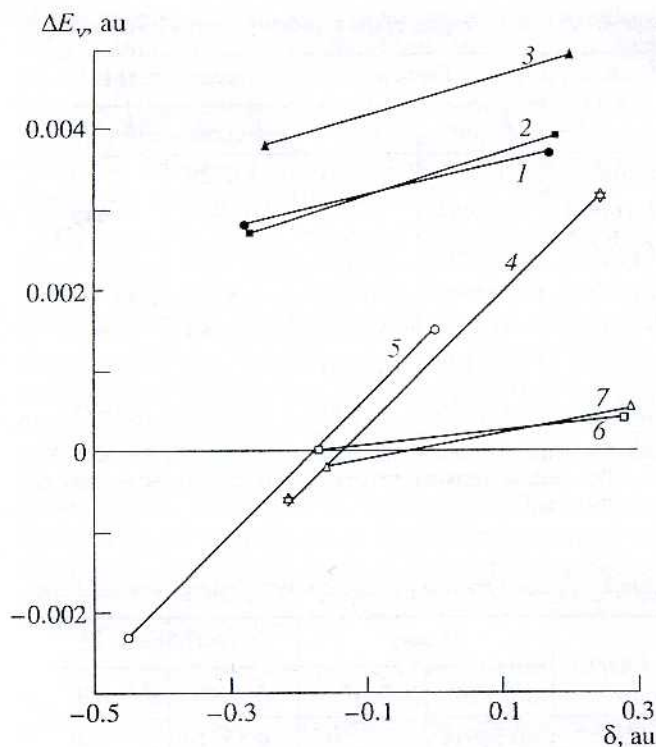


Fig. 1. Dependences of differences between theoretical and experimental energies of lower levels of the mercury atom on the parameter δ . (1) $^3P_0(6s6p)$; (2) $^3P_1(6s6p)$; (3) $^3P_2(6s6p)$; (4) $^1P_1(6s6p)$; (5) $^1S_0(6s^2)$; (6) $^3S_1(6s7s)$; (7) $^1S_0(6s7s)$ (see the text).

By solving this equation with different δ , we obtain $E_n(\delta)$. By comparing the theoretical spectrum with the experimental one, the optimum value of the shift can be chosen.

We chose the mercury atom as the first example. The atomic core $1s^2 \dots 5d^{10}$ was constructed in the V^N approximation. For two valence electrons, the complete overlap of configurations was made in the basis set including ten s , p , and d orbitals, seven f orbitals, and two g orbitals. Equation (18) was solved for the atomic levels $^1S_0(6s^2)$, $^3S_1(6s7s)$, $^1S_0(6s7s)$, $^3P_{0,1,2}(6s6p)$, and $^1P_1(6s6p)$. The valence energies obtained were compared with experimental values [12, 13]. Figure 1 shows the dependence of the difference between theoretical and experimental energies on δ .

As was expected, the absolute value of the MPT corrections to energies increases for $\delta < 0$ and decreases for $\delta > 0$. For $\delta = 0$, theoretical energies of all the levels prove to be somewhat overestimated. One can see from Fig. 1 that the position of the $^3P_1(6s6p)$ triplet rather weakly depends on δ ; thus it cannot be made closer to its experimental value by varying δ (this can be only achieved in the energy region where the operator Σ has poles). For the rest of the levels, the best agreement

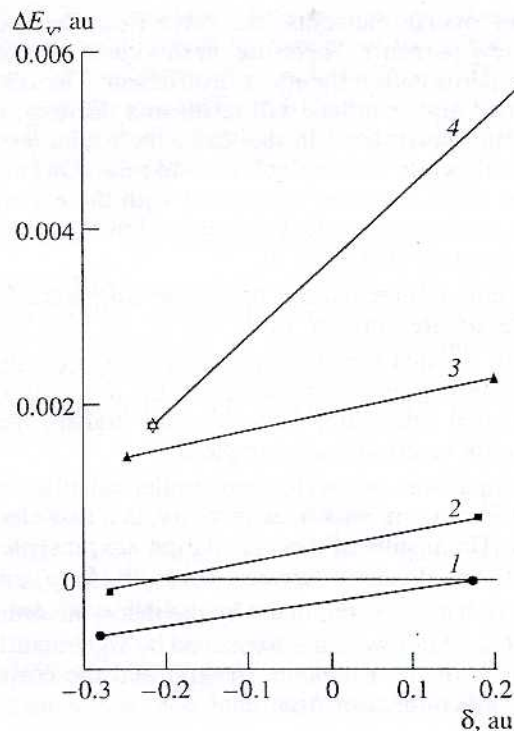


Fig. 2. Dependences of differences between theoretical and experimental energies of levels of the $6s6p$ configuration of the mercury atom on the parameter δ . The MPT correction $V'_{6p,6s,6s,6p}$ to the exchange integral is reduced by 30%. (1) $^3P_0(6s6p)$; (2) $^3P_1(6s6p)$; (3) $^3P_2(6s6p)$; (4) $^1P_1(6s6p)$.

with the experiment was achieved for $\delta \approx -0.175$ au. This shift is substantially lower than the value $\delta = -0.318$ au predicted by expression (14).

Let us now turn to the $^3P_1(6s6p)$ levels, whose position is poorly predicted by the theory. The reason for a large theoretical error is a very large correction to the exchange integral $V'_{6p,6s,6s,6p}$, which determines the distance between levels $^3P_1(6s6p)$ and $^1P_1(6s6p)$ in the one-configuration approximation (see, for example, section 17 in [14]). When the overlap of configurations is taken into account, the distance between the triplet and singlet levels decreases by 30%, but is still mainly determined by the same exchange integral. In the second order of the perturbation theory, the screening correction is determined by the matrix element $R_{6p,6s,6s,6p}$, to which a set of two-particle MPT diagrams corresponds (see details in [1]). The magnitudes of these matrix elements are

$$\text{Hg} : V'_{6p,6s,6s,6p} = 0.093 \text{ au}, \quad (19)$$

$$R_{6p,6s,6s,6p} = -0.019 \text{ au}.$$

One can see from (19) that the correction reduces the matrix element of the residual interaction by 20% (for

most other matrix elements, the correction does not exceed a few percent). Therefore, in this case, the second-order perturbation theory is insufficient. The consideration of higher orders will result in a decrease in the screening correction. In this case, the triplet level will descend, while the singlet level will raise. One can verify that to improve the agreement with the experiment, it is sufficient to reduce the correction $R_{6p, 6s, 6s, 6p}$ by approximately 30% (Fig. 2).

The results of calculations of the mercury atom for $\delta = -0.175$ are presented in Table 1.

One can see that the optimum choice of the parameter δ for the mercury atom improves the accuracy of the theoretical spectrum, however, the higher-order effects cannot be eliminated completely.

For comparison, we performed similar calculations for the barium atom, which, as mercury, is a two-electron atom. The results of this calculation are presented in Table 2. The distance between levels $^3P_1(6s6p)$ and $^1P_1(6s6p)$ in barium is predicted by the theory an order of magnitude better, which is explained by significantly lower values of the exchange integral and the corresponding screening correction:

$$\begin{aligned} \text{Ba} : V'_{6p, 6s, 6s, 6p} &= 0.057 \text{ au}, \\ R_{6p, 6s, 6s, 6p} &= -0.0086 \text{ au}. \end{aligned} \quad (20)$$

For this reason, the theoretical spectrum of barium agrees much better with the experiment (see calculations [2, 3]), and this agreement can be substantially improved by varying the parameter δ . Unlike mercury, for $\delta = 0$, the theory overestimates the valence energy, resulting in the positive optimum shift $\delta = 0.2$ for most levels and the zero shift for the levels of the $6s5d$ configuration. This means that expression (14), which yields in this case $\delta = -0.2$, is invalid for barium.

Finally, Table 3 presents the results of calculations of the thallium spectrum. In this case, the best agreement with the experiment was achieved when the effective Hamiltonian was calculated using the same valence energy $E_v = -1.64$ au for all the levels. This corresponds to the shift $\delta = -0.43$ au for the ground state and $\delta = -0.27$ au for the highest $6d_{5/2}$ state. The average shift is close to the value -0.38 au, which expression (14) yields. Note that the accuracy of the theoretical spectrum of thallium was improved, using the parameter E_v , by an order of magnitude compared to calculations [1].

DISCUSSION

One can see that the theory admits the use of various one-particle operators as the initial approximation. In the case of many valence electrons, the initial approximation can be determined by specifying δ from the condition (14). When the experimental spectrum is known, the best fit parameter δ can be found. In this case, the higher-order MPT corrections to the function are minimized. In this way, the accuracy of calculations

Table 1. Valence energies of the low-lying energy levels of Hg

Level	Theory		Experiment [13]	
	E_v , au	ΔE , cm^{-1}	E_v , au	ΔE , cm^{-1}
$^1S_0(6s^2)$	-1.0729	0	-1.0729	0
$^3P_0(6s6p)$	-0.8984	38300	-0.9014	37645
$^3P_1(6s6p)$	-0.8903	40080	-0.8933	39412
$^3P_2(6s6p)$	-0.8682	44930	-0.8722	44043
$^1P_1(6s6p)$	-0.8269	53990	-0.8265	54069
$^3S_1(6s7s)$	-0.7888	62350	-0.7888	62350
$^1S_0(6s7s)$	-0.7818	63890	-0.7816	63928

Note: The effective Hamiltonian was constructed for $\delta = -0.175$. This shift corresponds to the best fit of experimental valence energies E_v .

Table 2. Valence energies of the low-lying energy levels of Ba

Level	Theory		Experiment [12]	
	E_v , au	ΔE , cm^{-1}	E_v , au	ΔE , cm^{-1}
$^1S_0(6s^2)$	-0.55916	0	-0.55916	0
$^3D_1(6s5d)$	-0.51786	9064	-0.51800	9034
$^3D_2(6s5d)$	-0.51700	9254	-0.51717	9216
$^3D_3(6s5d)$	-0.51518	9653	-0.51543	9597
$^1D_2(6s5d)$	-0.50699	11451	-0.50724	11395
$^3P_0(6s6p)$	-0.50319	12284	-0.50327	12266
$^3P_1(6s6p)$	-0.50150	12656	-0.50518	12637
$^3P_2(6s6p)$	-0.49750	13533	-0.49758	13515
$^1P_1(6s6p)$	-0.47629	18188	-0.47863	18060

Note: The effective Hamiltonian was constructed for $\delta = 0$ for the levels of the $6s5d$ configuration and for $\delta = +0.2$ au for the rest of the levels. These shifts correspond to the best fit of experimental valence energies E_v .

Table 3. Valence energies of the low-lying energy levels of Tl

Level	Theory		Experiment [12]	
	E_v , au	ΔE , cm^{-1}	E_v , au	ΔE , cm^{-1}
$6p_{1/2}$	-2.07205	0	-2.07221	0
$6p_{3/2}$	-2.03647	7808	-2.03670	7793
$7s_{1/2}$	-1.95144	26472	-1.95157	26478
$7p_{1/2}$	-1.91636	34169	-1.91657	34160
$7p_{3/2}$	-1.91180	35170	-1.91201	35161
$6d_{3/2}$	-1.90735	36148	-1.90764	36118
$6d_{5/2}$	-1.90701	36222	-1.90727	36200

Note: The effective Hamiltonian was constructed for the energy $E_v = -1.64$ au, which corresponds to the best fit of experimental values of ΔE .

of the atomic amplitudes can be improved, including the amplitudes for which the direct experimental data are absent. Of most interest is the use of the method of effective Hamiltonian for precise calculations of effects of parity nonconservation, which are necessary for verifying the agreement between predictions of a standard model and atomic experiments [9, 10, 15, 16].

Comparison of the results of calculations of mercury, barium, and thallium atoms shows that the accuracy of calculations is the worst for mercury and the best for thallium. The typical value of the theoretical error is $\sim 600 \text{ cm}^{-1}$ for mercury, $\sim 100 \text{ cm}^{-1}$ for barium, and $\sim 20 \text{ cm}^{-1}$ for thallium. The reason for the improvement of the accuracy of calculations in passing from mercury to thallium is, probably, the increase in the excitation energy of the atomic core, which equals 0.398, 0.756, and 0.873 au for these atoms, respectively. Indeed, an increase in the excitation energy of the atomic core should result in the increasing rate of convergence of the MPT series and the decreasing role of higher-order corrections.

The increase in the accuracy of calculations in passing from two-electron to three-electron atoms allows one to expect good results also for the atoms containing more than three valence electrons, for which the excitation energy of the atomic core is even higher. In this case, the main problem will be not the construction of the effective Hamiltonian but the solution of the wave equation in the valence space, whose size very rapidly increases with increasing number of valence electrons. Nevertheless, the valence problem for four electrons can be still solved with sufficient accuracy.

As was shown above, the choice of the parameter δ , with the help of expression (14), is far from optimum for mercury and barium, but is significantly closer to it for thallium. One can expect that this expression will be even more appropriate in the case of four-electron atoms such as lead.

CONCLUSIONS

The results of the paper can be briefly formulated as follows:

(i) The subtraction of the parameter δ from the operator of the residual interaction is equivalent, with an accuracy of the higher-order terms of the perturbation energy, to the calculation of the effective Hamiltonian for the energy $E - \delta$.

(ii) The parameter δ can be used as a fitting parameter to improve the agreement with the experiment. When the number of valence electrons is greater than two, the value of δ can be chosen on theoretical grounds, by setting the matrix element of the residual interaction for one of the atomic states equal to zero. Such a choice of the parameter δ makes the variant of the perturbation theory used here similar to the Rayleigh-Schrödinger perturbation theory.

(iii) The absolute value of the optimum shift δ increases with increasing number of valence electrons, while the derivative $dE_{\text{theor}}/d\delta$ decreases. This allows one to use the same effective Hamiltonian for groups of the adjacent levels, resulting in a significant simplification of calculations.

ACKNOWLEDGMENTS

M.G. Kozlov thanks V. Dzuba and G. Gribakin for numerous discussions of the results of this paper. This work was supported by the Russian Foundation for Basic Research, project no. 98-02-17663. S.G. Porsev thanks the mayor of St. Petersburg for financial support.

REFERENCES

1. Dzuba, V.A., Flambaum, V.V., and Kozlov, M.G., *Pis'ma Zh. Tekh. Fiz.*, 1996, vol. 73, p. 844; *Phys. Rev. A*, 1996, vol. 54, p. 3948.
2. Kozlov, M.G. and Porsev, S.G., *Zh. Eksp. Teor. Fiz.*, 1997, vol. 111, p. 838.
3. Dzuba, V.A. and Johnson, W.R., *Phys. Rev. A*, 1998, vol. 57, p. 2459.
4. Mosyagin, N.S., Kozlov, M.G., and Titov, A.V., *E-print: Physics*, 9804013, 1998.
5. Dzuba, V.A., Kozlov, M.G., Porsev, S.G., and Flambaum, V.V., *Zh. Eksp. Teor. Fiz.*, 1998, vol. 114, no. 5, p. 1636.
6. Kozlov, M.G., Titov, A.V., Mosyagin, N.S., and Souchko, P.V., *Phys. Rev. A*, 1997, vol. 56, no. 5, pp. R3326-R3329.
7. Mosyagin, N.S., Kozlov, M.G., and Titov, A.V., *J. Phys. B: At., Mol. Opt. Phys.*, 1998, vol. 31, p. L763.
8. Lindgren, I. and Morrison, J., *Atomic Many-Body Theory*, Berlin: Springer-Verlag, 1985, 2nd ed.
9. Meekhof, D.M. *et al.*, *Phys. Rev. A*, 1995, vol. 52, p. 1895.
10. Macpherson, M.J.D. *et al.*, *Phys. Rev. Lett.*, 1991, vol. 67, p. 2784.
11. Thouless, D.J., *The Quantum Mechanics of Many-Body Systems*, New York: Academic, 1972, 2nd ed. Translated under the title *Kvantovaya mekhanika sistem mnogikh chastits*, Moscow: Mir, 1975.
12. Moore, C.E., *Atomic Energy Levels*, Circ. no. 467, Washington: Natl. Bur. Stand. US, 1958.
13. Radtsig, A.A. and Smirnov, B.M., *Spravochnik po atomnoi i molekulyarnoi fizike* (A Handbook on Atomic and Molecular Physics), Moscow: Atomizdat, 1980.
14. Sobel'man, I.I., *Vvedenie v teoriyu atomnykh spektrov* (Introduction to the Theory of Atomic Spectra), Moscow: Fizmatgiz, 1963.
15. Edward, N.H., Phipp, S.J., Baird, P.E.G., and Nakayama, S., *Phys. Rev. A*, 1995, vol. 74, p. 2654.
16. Vetter, P.A. *et al.*, *Phys. Rev. A*, 1995, vol. 74, p. 2658.

Translated by M. Sapozhnikov