The Rydberg series for the doubly excited states of the helium atom

A. K. Kazanskiĭ and V. N. Ostrovskiĭ

Leningrad State University
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The doubly excited states of a two-electron atom are considered within the framework of perturbation theory constructed in terms of the interelectron interaction. It is assumed that one of the electrons is excited to a much higher level than the other. This allows the use of the multipole expansion of the interaction. The contributions to the level shift from the dipole term (including the second-order perturbation theory correction) and the quadrupole term (in first order) are represented in the form of matrix elements of some equivalent operators. The latter are expressed in terms of the integrals of motion for the unperturbed Coulomb problem. The large magnitude L of the total orbital angular momentum of the atom serves as the parameter of the expansion obtained. The breakdown of the single-configuration approximation, an alternative classification of the states, and the additional integrals of the motion are discussed. It is shown that the problem of quantization in the asymptotic limit in question is effectively a one-dimensional problem. Simple explicit formulas are obtained for the quantum defects of the Rydberg series, which converge to the ionic energy levels with principal quantum numbers 2 and 3. The results are compared with data obtained in numerical computations for $L = 3$. It is shown that account should also be taken in this case of the contribution of that region of configuration space which corresponds to the penetration of the highly excited electron to the nucleus.

1. INTRODUCTION

The fundamental interest in the investigation of the doubly excited states of a two-electron atom is due to the fact that we cannot use in this important case of the quantum three-body problem the standard—in the theory of the atom—effective central field approximation and the fact that the interelectron correlations play an extremely important role (see, for example, the reviews in Refs. 1 and 2). This does not allow us to describe the states of the atom with the aid of the single-electron configuration, in which definite values of the principal n_i and orbital angular momentum l_i quantum numbers are ascribed to each (ith) electron.

The single-electron configuration approximation can break down even in the case when one of the electrons is much more highly excited than the other.[3] In this case it is natural to assume that one of the electrons (the first) is, on the average, located much farther away from the atomic nucleus than the other, and use the multipole expansion for the interaction potential:

$$\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} - \frac{1}{r_1} = \frac{\mathbf{r}_1 \mathbf{r}_2}{r_1^3} + \frac{3(\mathbf{r}_1 \mathbf{r}_2)^2 - r_1^2 r_2^2}{2r_1^5} + O\left(\frac{1}{r_1^4}\right). \quad (1)$$

Here the $\mathbf{r}_i$ are the radius vectors of the electrons with respect to the nucleus. The electrons are assumed to be distinguishable, since they reside in different regions of configuration space: the exchange effects are weak, and are not considered below (they can be taken into account separately).

The dipole approximation, in which only the first term in the right member of (1) is taken into account, has been considered in detail in a number of papers[4–6] under the assumption that the second (inner) electron resides in a definite layer, i.e., possesses a definite principal quantum number n_2. Then the problem reduces to one of diagonalization and investigation of the operator Λ introduced in Refs. 4 and 6.

In the present paper we construct a perturbation theory in terms of the interaction (1). This allows us to take account of the virtual excitations of the inner electron, and uniformly consider the contribution of the quadrupole term in (1) (this contribution has been found by Nikitin[7] for certain states). Recently Belov and Khveshchenko[8] developed a classical perturbation theory, for the applicability of which we must assume not only the condition $n_1 \gg n_2$ used by us, but also the extremely restrictive—from the standpoint of applications—conditions $n_2 \gg 1$ (the contribution of the virtual excitations of the inner electron is then neglected).

A fundamental feature in the analysis of the doubly excited states of the helium atom within the framework of perturbation theory in terms of the electron-electron interaction is the strong degeneracy of the unperturbed states, which arises because of the unique degeneracy in the single-electron hydrogen-like atom. The lifting of the degeneracy leads to the appearance of states in which the motions of the electrons are highly correlated. For the construction of the correct zero-order functions, it is convenient to represent the terms of the perturbation theory series for the energy level shift in the form of matrix elements of some equivalent operators.

In the present paper we are able to do this for the second-order perturbation theory contribution from the dipole interaction by evaluating the corresponding sum exactly. We also take account of the quadrupole term in first order. In both cases the equivalent operators are constructed from the integrals of motion for the unperturbed Coulomb problem: the orbital angular momentum vector and the Runge-Lenz vector. A similar approach has been used before to compute the energy levels of the hydrogen atom in crossed electric and magnetic fields,[9] and also to investigate single-electron[10,11] and two-electron[4,6] systems.

2. THE EQUIVALENT OPERATORS

The perturbation theory is constructed with the unperturbed Coulomb wave functions $|n_i l_i m_i\rangle$, with the effective charges for the inner- and outer-shell electrons equal respectively to Z and $Z - 1$, where Z is the nuclear charge, and the charge for the outer electron takes account of the screening. For the dipole interaction $\hat{V}_d = \mathbf{N}_1 \cdot \mathbf{r}_2 / r_1^2$ the equivalent operator

$$U_{d1} = -3n_2 \mathbf{N}_1 \mathbf{A}_2 / 2Z r_1^2, \qquad (2)$$

where $\mathbf{N}_1 = \mathbf{r}_1 / r_1$ is found with the aid of the operator identity[9]

$$\mathbf{r}_2 = -3n_2 \mathbf{A}_2 / 2Z, \qquad (3)$$

which is valid within the boundaries of the n_2 layer. Here $\mathbf{A}_2$ is the Runge-Lenz vector for the inner electron:

$$\mathbf{A}_2 = (-2H_{02})^{-1/2} \{ \tfrac{1}{2} ([\mathbf{p}_2 \mathbf{l}_2] - [\mathbf{l}_2 \mathbf{p}_2]) - Z\mathbf{r}_2 / r_2 \}, \\ H_{02} = -\tfrac{1}{2} \nabla_2^2 - Z/r_2, \qquad (4)$$

where $\mathbf{p}_i$ and $\mathbf{l}_i$ are respectively the momentum and orbital angular momentum operators for the ith electron. It is easy to see that, in the subspace of wave functions with a definite n_2 value, all the matrix elements of the dipole interaction vanish by virtue of the following identity for the Coulomb radial wave functions[12] $R_{nl}(r_1)$:

$$\int_0^\infty R_{nl}(r_1) r_1^{-k} R_{nl+a}(r_1) r_1^2 \, dr_1 = 0 \quad \text{for} \quad 2 \leqslant k \leqslant a+1. \qquad (5)$$

The group-theoretical nature of this identity is discussed in Ref. 13.

The dipole interaction makes a nonvanishing contribution to the energy level shift in second order perturbation theory. This contribution can be represented as the following operator's contribution averaged over the unperturbed state having given n_1, n_2 and arbitrary l_i, m_i:

$$U_{d2} = \sum_{\substack{n_1' l_1' m_1' \\ n_2' l_2' m_2'}} \frac{\hat{V}_d |n_1' l_1' m_1' n_2' l_2' m_2'\rangle\langle n_1' l_1' m_1' n_2' l_2' m_2'| \hat{V}_d}{E_{n_1} + E_{n_2} - E_{n_1'} - E_{n_2'}}, \qquad (6)$$

$$(n_1' n_2') \neq (n_1, n_2), \quad E_{n_1} = -\frac{(Z-1)^2}{2n_1^2}, \quad E_{n_2} = -\frac{Z^2}{2n_2^2}.$$

Let us split the sum over the intermediate states that enters into the expression (6) into two parts: $U_{d2} = U_{d2}^{(1)} + U_{d2}^{(2)}$. Let the first part ($U_{d2}^{(1)}$) contain the terms for which the inner electron resides in the initial n_2 layer. To compute it, let us use the operator identity (3), as well as the sum rule derived in the Appendix for the single-electron Coulomb states:

$$U_{d2}^{(1)} = \frac{9n_2^2}{8Z^2(Z-1)} \frac{1}{r_1^3} [3(\mathbf{N}_1 \mathbf{A}_2)^2 - \mathbf{A}_2^2 - \mathbf{l}_1 \mathbf{l}_2]. \qquad (7)$$

Let us compute the second part ($U_{d2}^{(2)}$) of the sum approximately, assuming the energy of the virtual transition of the outer electron is negligible compared to the analogous quantity for the inner electron. Then the summation over the outer-electron states can be carried out with the aid of the completeness relation, and the sum over the inner-electron states coincides with the sum evaluated by Solov'ev[11]:

$$U_{d2}^{(2)} = (n_2^4 / 16 Z^2 r_1^4) [5n_2^2 + 31 + 24 l_2^2 - 21(\mathbf{N}_1 \mathbf{l}_2)^2 + 9(\mathbf{N}_1 \mathbf{A}_2)^2]. \qquad (8)$$

The quadrupole term in the interaction (1) makes a nonzero contribution to the energy-level shift even in first-order perturbation theory. The corresponding equivalent operator can be found with the aid of the operator identity (A.4) derived in the Appendix:

$$U_{q1} = (3n_2^2 / 4Z^2 r_1^3) [5(\mathbf{N}_1 \mathbf{A}_2)^2 - \tfrac{5}{3} \mathbf{A}_2^2 - (\mathbf{N}_1 \mathbf{l}_2)^2 + \tfrac{1}{3} \mathbf{l}_2^2]. \qquad (9)$$

3. CLASSIFICATION OF THE STATES

To determine the correct perturbation-theory functions, we must diagonalize on the degenerate states the total equivalent operator $U_{d2}^{(1)} + U_{d2}^{(2)} + U_{q1}$, taking account in the process of the existence of exact integrals of the motion: the atom's total orbital angular momentum $\mathbf{L} = \mathbf{l}_1 + \mathbf{l}_2$ and the parity. Let us note that the r_1 dependence of the operator $U_{d2}^{(1)}$ is formally responsible for the charge-quadrupole interaction, and coincides with the corresponding dependence of the operator U_{q1}. For the $U_{d2}^{(2)}$ operator the r_1 dependence corresponds to the polarization interaction (the polarization of the inner electron by the outer electron).

The operators $U_{d2}^{(1)}$ and U_{q1} are, in accordance with the identity (5), diagonal in the quantum number l_1, which allows us to rewrite them by replacing r_1^{-3} by the corresponding matrix element and using the equivalent (in the subspace of the states with a given l_1) operator for the tensor[14] $N_{1i} N_{1k} - \delta_{1k}/3$:

$$U_{d2}^{(1)} = \frac{9n_2^2(Z-1)^2}{4Z^2 n_1^3} \frac{2l_1^2(n_2^2 - 1 + l_1^2 - L^2) - 6(\mathbf{A}_2 \mathbf{l}_1)^2 + 3l_1 l_2}{l_1(l_1+1)(2l_1-1)(2l_1+1)(2l_1+3)}, \qquad (10)$$

$$U_{q1} = -\frac{n_2^2(Z-1)^3}{Z^2 n_1^3} \frac{15(\mathbf{A}_2 \mathbf{l}_1)^2 - 5l_1^2 \mathbf{A}_2^2 - 3(\mathbf{l}_1 \mathbf{l}_2)^2 + l_1^2 l_2^2}{l_1(l_1+1)(2l_1-1)(2l_1+1)(2l_1+3)}. \qquad (11)$$

For the multipole expansion of the interaction in the formula (1) to be applicable, not only the condition $n_1 \gg n_2$, but also the condition $l_1 \sim L \gg n_2 - 1$ should be fulfilled.[5] It is not difficult to determine the order of smallness of the operators under consideration:

$$U_{d2}^{(1)} \sim L^{-2}, \quad U_{q1} \sim L^{-3}, \quad U_{d2}^{(2)} \sim L^{-5}.$$

It is precisely this relation that allows us to restrict ourselves to the quadrupole interaction in first order perturbation theory, and also to treat the operator $U_{d2}^{(2)}$ as a small correction.[1] Other corrections to the energy (the operator V_d in fourth order perturbation theory, the quadrupole term in the interaction (1) in second order perturbation theory, as well as the third order perturbation theory with mixed dipole and quadrupole interactions[2]) are of the order of L^{-4}. Since these corrections are not computed in the present paper, the $U_{d2}^{(2)}$ term will be ignored below.

Thus, the quantum number l_1 is, to a high degree of accuracy (without allowance for the inner-electron polarization), a "good" quantum number, i.e., the operator l_1^2 serves as an approximate integral of motion. Since the quantum number l_2 can take on different values at given values of L, l_1, and n_2, an additional integral is needed for a unique determination of the states. If we consider only the dipole interaction, then, as can be seen from (11), the operator $(\mathbf{A}_2 \mathbf{l}_1)^2$ serves as such an integral of motion in addition to l_1^2. It is precisely such integrals that are proposed and investigated in Refs. 5 and 6. The operator $(\mathbf{A}_2 \mathbf{l}_1)^2$ in its general form can be diagonalized in the asymptotic limit of large L.

When allowance is made for the quadrupole interaction, the role of the additional integral of motion is played by that part of the sum $U_{d2}^{(1)} + U_{q1}$ which contains some other operators besides l_1^2 and L^2. Dropping the constant factor, carrying out simple identity transformations, and taking account of the fact that

$$l_1 l_2 = \tfrac{1}{2}(L^2 - l_1^2 - l_2^2),$$

we obtain the additional integral

$$[9+10(Z-1)](A_2 l_1)^2 + 2(Z-1)[2l_1^2 l_2^2 - (l_1 l_2)^2], \qquad (12)$$

which, in its general form, can no longer be diagonalized. In the basis of the single-electron configurations, the problem of the diagonalization of this operator reduces to trinomial recurrence formulas, which can be investigated in the semi-classical approximation with the aid of the procedure developed by Braun.[15] Let us note, however, that the numerical values of the coefficients in the expression for the operator (12) are such that its eigenfunctions are usually close to the eigenfunctions of $(A_2 l_1)^2$ (see also Sec. 4).

The expressions (10) and (11), after they have been expanded in the large quantity $L \sim l_1$ up to terms of the order of $O(L^{-3})$ inclusively, coincide with the formulas obtained in Ref. 8 for the corrections to the effective Hamiltonian. It should, however, be noted that the qualitative discussion in the cited paper is based on the assertion that the various terms in the multipole expansion of the interaction make (in the various perturbation theory orders) to the energy of the states contributions of different orders in the large principal quantum number n_1 of the outer electron. Indeed, as can be seen, for example, from the formulas (10), (11), and (8), in terms of $n_1 \to \infty$ all the corrections are of the order of n_1^{-3} (a fact which already follows from the normalization of the Coulomb wave functions), and they are ordered only in the parameter L^{-1}.

4. THE RYDBERG SERIES FOR THE DOUBLY EXCITED STATES

The doubly excited states under consideration form Rydberg series within which the principal quantum number n_1 of the outer electron varies, while the remaining quantum numbers remain constant. As n_1 increases, the energy levels in a series converge to a limit characterized by the energy of the single-electron ion in the state with principal quantum number n_2 (Refs. 5 and 7). The quantum defects $\delta_{n_2 \gamma}$ of the series are usually used to describe the positions of the energy levels $E_{n_1 n_2 \gamma}$:

$$E_{n_1 n_2 \gamma} = -\frac{Z^2}{2n_2^2} - \frac{(Z-1)^2}{2(n_1 + \delta_{n_2 \gamma})^2}, \qquad (13)$$

where γ denotes the set of all the remaining quantum numbers. The n_1 dependence of the operators (10) and (11) conforms precisely to an approximation of the quantum defect $(\Delta E_{n_1 n_2 \gamma} \sim n_1^{-3})$.

For given values of the quantum numbers L, l_1, n_1, and n_2 ($|L - l_1| \leqslant n_2 - 1$), the quantum number l_2 can take on values ranging from $|L - l_1|$ to $n_2 - 1$. This determines the dimensionality of the basis in which the operator (12) should be diagonalized for the purpose of carrying out a classification of the Rydberg series (or the energy levels in them). The classification of the atomic states according to

parity π, which in our case is determined by the parity of l_2, further lowers the dimensionality of the basis.

In particular, for $n_2 = 2$, only one state corresponds to a given set of L, l_1, and π values, and no diagonalization is necessary, it being sufficient to compute only the diagonal matrix elements of the equivalent operators. For $n_2 = 3$ the situation is similar for all the states, with the exception of the $l_1 = L$, $\pi = (-1)^L$ case, in which we have to diagonalize a 2×2 matrix. The last case constitutes the simplest example of strong intermixing of single-electron configurations (see Sec. 1).

Thus, in the case of the series with $n_2 = 2$ and $n_2 = 3$, it is possible to obtain for the quantum defects $\delta_j^\pi (j = L - l_1)$ analytic formulas having the following form:

$$\delta_1^{\pi_1} = -\frac{18}{Z^2(2L-1)(2L+1)} + \frac{12(Z-1)}{Z^2 L(2L-3)(2L+1)}.$$

$$\delta_0^{\pi_1} = O(L^{-4}), \qquad (14)$$

$$\delta_{-1}^{\pi_1} = \frac{18}{Z^2(2L+1)(2L+3)} + \frac{12(Z-1)}{Z^2(L+1)(2L+1)(2L+5)};$$

for the case $n_2 = 2$, $\pi_1 = (-1)^L$;

$$\delta_0^{\pi_2} = -\frac{12(Z-1)(4L^2+4L-1)}{Z^2 L(L+1)(2L-1)(2L+1)(2L+3)}; \qquad (15)$$

for the case $n_2 = 2$, $\pi = (-1)^{L+1}$;

$$\delta_2^{\pi_1} = -\frac{81}{Z^2(2L-1)(2L-3)}$$

$$+ \frac{36(Z-1)(4L-7)}{Z^2(L-1)(2L-1)(2L-3)(2L-5)},$$

$$\delta_1^{\pi_1} = -\frac{81(L-1)}{2Z^2 L(2L-1)(2L+1)}$$

$$+ \frac{18(Z-1)(8L-9)}{Z^2 L(2L-3)(2L-1)(2L+1)},$$

$$\delta_{0\pm}^{\pi_1} = \frac{9[a \pm (a^2+b^2)^{1/2}]}{4Z^2 L(L+1)(2L-1)(2L+1)(2L+3)}, \qquad (16)$$

$$a = 9(4L^2+4L+3) - 4(Z-1)(8L^2+8L-21),$$
$$b = 4[9+10(Z-1)][2L(L+1)(2L-1)(2L+3)]^{1/2},$$

$$\delta_{-1}^{\pi_1} = \frac{81(L+2)}{2Z^2(L+1)(2L+1)(2L+3)}$$

$$+ \frac{18(Z-1)(8L+15)}{Z^2(L+1)(2L+1)(2L+3)(2L+5)},$$

$$\delta_{-2}^{\pi_1} = \frac{81}{Z^2(2L+3)(2L+5)}$$

$$+ \frac{36(Z-1)(4L+11)}{Z^2(L+2)(2L+3)(2L+5)(2L+7)};$$

for the case $n_2 = 3$, $\pi = (-1)^L$; and

$$\delta_1^{\pi_2} = -\frac{81(L-1)}{2Z^2 L(2L-1)(2L+3)}$$

$$- \frac{18(Z-1)(4L^2+11L-21)}{Z^2 L(L-1)(2L-3)(2L-1)(2L+1)},$$

$$\delta_0^{\pi_2} = -\frac{81}{2Z^2 L(L-1)(2L+1)}$$

$$- \frac{18(Z-1)(10L^2+16L-9)}{Z^2 L(L+1)(2L-1)(2L+1)(2L+3)}. \qquad (17)$$

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$$\delta_{-1}{}^{\pi_2} = \frac{81(L+2)}{2Z^2(L+1)(2L+1)(2L+3)} - \frac{18(Z-1)(4L^2-3L-28)}{Z^2(L+1)(L+2)(2L+1)(2L+3)(2L+5)}$$

for the case $n_2 = 3$, $\pi_2 = (-1)^{L+1}$.

The above-presented expressions[3] include terms of order not higher than L^{-3} and, in particular, do not take account of the polarization effects. As has already been noted, the case $n_2 = 3$, $\pi = (-1)^L$, and $j = 0$ contains two series, the quantum defects of which are further labeled by the indices $\pm$. Since the exchange is ignored in the present paper, the quantum defects obtained characterize the spin-averaged positions of the energy levels.

Table I contains the quantum-defect values computed with the aid of the above-presented formulas for the Rydberg series of the helium atom (the column a). The value $L = 3$ chosen for the total orbital angular momentum of the atom is not large enough for a safe application of the asymptotic theory developed in the present paper (with the general condition of applicability $L \gg n_2 - 1$), but is the greatest value for which other authors have carried out systematic calculations. In the papers cited in Ref. 16 Feshbach's projection operator method is used to compute the lowest levels ($n_1 \leqslant 6$ or 7) of the series under consideration. The quantum defects found from these data are given in the column c in Table I (the series designations used in Ref. 16 are also indicated). It should be noted that the correlation of these δ values with the quantum number j is not always unique. The identification adopted by us for $j = 1$, 2 ($n_2 = 3$, $\pi = -1$) differs from the one used by Nikitin,[7] the results of whose calculations are presented in the column e. We also give for some series the quantum defects (the column d), which were ex-

tracted by us from the results of energy level ($n_1 \leqslant 4$ or 5) calculations carried out by the complex coordinate rotation method.[17]

On the whole the table shows a clear improvement in the agreement with the numerical calculation for those states for which the quantum number l_1 assumes the greatest admissible (for a given L) value, a circumstance which is clearly favorable for the application of the asymptotic theory. As is to be expected, there is poor agreement in the $n_2 = 3$ case for the quantum defects δ^o_2, δ^o_1, and δ^o_{0+} (in the first of these series for $L = 3$ the orbital angular momentum of the outer electron is even smaller than that of the inner electron). Let us note that, in these cases, as noted in Ref. 7, the exchange level splitting, which is ignored in the present paper, is relatively large. The very good agreement obtained for the quantum defects δ^e_1 and δ^o_{0-} is, as follows from further analysis, accidental.

The configuration mixing data for $n_2 = 2$ in the numerical calculation reported in Ref. 16 confirm that l_2 is a good quantum number.

The series with quantum defects δ^o_{0+} and δ^o_{0-} are superpositions of single-electron configuration states with comparable weights. Thus, for the first of these series the amplitudes of the $(l_1, l_2) = (3, 0)$ and $(l_1, l_2) = (3, 2)$ configurations are respectively equal to 0.73 and 0.68.

As noted in the discussion in Sec. 3, the numerical coefficients in the additional integral of motion (12) are such that we can approximate the operator classifying the states by $(A_2 l_1)^2$. Then in order to approximately determine the quantum defects, we must compute the diagonal matrix elements of the equivalent operators with the eigenfunctions of the operators $l_1{}^2$ and $(A_2 l_1)^2$. For $L = 3$ and $n_2 = 3$ the thus obtained quantum defects δ^o_{0+} differ from the values calcu-

TABLE I. Quantum defects of the Rydberg series for the doubly excited states of a helium atom with total orbital angular momentum $L = 3$.

	(l_1, l_2)	a	b	c	e
			$n_2 = 2$		
δ^o_1	(2,1)	−0.0810	−0.108	−0.154(a)	−0.10
δ^o_0	(3,0)	0	−0.002	−0.014(b)	−0.007
δ^o_{-1}	(4,1)	0.0812	0.0812	0.0766(c)	0.08
δ^e_0	(3,1)	−0.0373	−0.0372	−0.0454(a)	−0.04

	(l_1, l_2)	a	b	c	d	e
				$n_2 = 3$		
δ^o_2	(1,2)	0.15	−0.873	−0.785(b)	−0.864	0.006
δ^o_1	(2,1)	0.0214	−0.365	−0.519(a)	−0.572	−0.62
δ^o_{0+}	(3,0)	−0.349	−0.347	−0.373(c)	−0.411	−0.35
δ^o_{0-}	(3,2)	0.396	0.299	0.052(d)	0.056	0.36
δ^o_{-1}	(4,1)	0.264	0.255	0.186(e)	—	0.25
δ^o_{-2}	(5,2)	0.237	0.237	0.246(f)	—	0.22
δ^e_1	(2,2)	−0.536	−0.477	−0.549(a)	−0.603	−0.51
δ^e_0	(3,1)	−0.338	−0.324	−0.300(b)	−0.345	−0.33
δ^e_{-1}	(4,2)	0.201	0.199	0.122(c)	—	0.19

Note: a) Computed from the formulas (14)–(17) of the present paper; b) computed from the same formulas, but with account taken of the correction for the penetration of the highly excited electron to the nucleus; c) results of numerical calculation reported in Ref. 16; d) results of numerical calculation reported in Ref. 16; d) results of numerical calculation reported in Ref. 17; and e) results of asymptotic calculation reported in Ref. 7.

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lated from the formulas (16) only in the fourth significant digit.

The approach adopted here can be developed further by carrying out a more accurate asymptotic expansion of the spectrum in powers of the parameter L^{-1}. Let us note that the expansion coefficients can be expressed in terms of the matrix elements, which diverge at insufficiently large values of l_1.

Of greater importance at not very large L values is allowance for the fact that the expansion (1) is not valid in that region of configuration space where the highly excited electron penetrates closer to the nucleus than the inner electron, i.e., in the region where $r_2 > r_1$. Since the first electron moves rapidly in this region, we can neglect its effect on the character of the interelectron correlations, and assume that the mixing of the single-electron configurations is described by the above-developed approximation. Then the effect of the penetration of the outer electron to the nucleus on the energy of the states can be taken into account in first order, taking as the perturbation the difference between the exact interaction (the left-hand side of the formula (1)) and its approximation (the right-hand side of (1)). Thus, the monopole part of this perturbation has the form $1/r_> - 1/r_1$, where $r_> = \max(r_1, r_2)$. As the zeroth-approximation wave functions, over which the averaging is carried out, let us, as has already been stated, take the functions obtained upon the diagonalization of the interaction $U_{d2}^{(1)} + U_{q1}$.

The contribution of the region $r_2 > r_1$ to the level shift is exponentially small[4] in the large parameter L. Allowance for it along with the first terms of the power expansion generated by the region $r_1 > r_2$ can be justified by the fact that these contributions have physically different natures, and are determined by different regions of configuration space.

The column b in Table I contains the quantum defects computed with account taken of the above-described correction for the penetration of the highly excited electron to the nucleus. The correction was found with allowance made for the monopole and quadrupole parts of the interaction (the dipole term makes no contribution). The details of the calculation are given in the Appendix. For $n_2 = 2$ the correction is small for all the series. For $n_2 = 3$ allowance for the correction makes the values of all the quantum defects reasonable, although the above-noted accidental agreement with the numerical calculation disappears. The worst agreement occurs in the case of the quantum defect δ_0^0 ; at large values of l_1 the role of the correction is minor, and we obtain the best agreement with the numerical calculations.

5. CONCLUSION

Thus, the limitations on the validity of the asymptotic theory at not too large values of the total angular momentum L of the atom arise not because of the neglect of the next terms of the expansion in L^{-1}, but because of the role of the penetration of the highly excited electron into the region close to the nucleus. As can be seen from a comparison with the results of the numerical calculations, the agreement is good when allowance for the indicated region yields a small correction. In the opposite case the nature of the configuration mixing can differ significantly from the nature of the mixing permitted by the asymptotic theory (cf., for example, the description[2] of the mixing for $n_1 \simeq n_2$).

In conclusion, let us note the importance of the following aspect of our result. Since the effective asymptotic Hamiltonian $U_{d2}^{(1)} + U_{q1}$ commutes with l_1^2 , the problem of its diagonalization is a one-dimensional one (it reduces to a set of trinomial recurrence formulas). Thus, in the present approximation the system turns out to be integrable in both the semiclassical[8] and quantum approaches. Apparently, after the diagonalization of this Hamiltonian, the degeneracy in l_1 can only be accidental, and, therefore, from the qualitative standpoint, the spectrum of the complete problem possesses all the properties of the spectrum of integrable systems.

APPENDIX

1. Let us denote by $|n_1 l_1 m_1\rangle$ the eigenfunctions of the unperturbed Coulomb Hamiltonian

$$H_{01} = -\tfrac{1}{2}\nabla_1^2 - (Z-1)/r_1.$$

Using the commutator

$$[H_{01}, \, \mathbf{p}_1 \mathbf{A}_2] = i(Z-1)\mathbf{r}_1 \mathbf{A}_2/r_1^3,$$

we obtain the following relation between the matrix elements:

$$(E_{n_1'} - E_{n_1})\langle n_1' l_1' m_1' | \mathbf{p}_1 \mathbf{A}_2 | n_1 l_1 m_1\rangle$$
$$= i(Z-1)\langle n_1' l_1' m_1' | (\mathbf{r}_1 \mathbf{A}_2)/r_1^3 | n_1 l_1 m_1\rangle, \qquad (A.1)$$

where $H_{01}|n_1 l_1 m_1\rangle = E_{n_1}|n_1 l_1 m_1\rangle$. The operator $\mathbf{A}_2$ does not act on the coordinates of the first electron (but acts on those of the second). Using the obtained identity, we can reduce the second order perturbation theory sum to the completeness relation for the basis $|n_1 l_1 m_1\rangle$, and this yields the sum rule

$$\sum_{\substack{n_1' l_1' m_1' \\ n_1' \neq n_1}} \left\{ \left\langle n_1 l_1 m_1 \left| \frac{\mathbf{r}_1 \mathbf{A}_2}{r_1^3} \right| n_1' l_1' m_1' \right\rangle \right.$$

$$\times \left\langle n_1' l_1' m_1' \left| \frac{\mathbf{r}_1 \mathbf{A}_2}{r_1^3} \right| n_1 \tilde{l}_1 \tilde{m}_1 \right\rangle$$

$$\times (E_{n_1} - E_{n_1'})^{-1} \Bigg\}$$

$$= \frac{1}{2i(Z-1)} \left\langle n_1 l_1 m_1 \left| \left[\mathbf{p}_1 \mathbf{A}_2, \frac{\mathbf{r}_1 \mathbf{A}_2}{r_1^3} \right] \right| n_1 \tilde{l}_1 \tilde{m}_1 \right\rangle . \qquad (A.2)$$

Also, taking account of the commutation relation $[A_{2i}, A_{2j}] = i\varepsilon_{ijk} l_{2k}$ for the components of the Runge-Lenz vector, we find that the values of the sum (A.2) can be obtained by computing the matrix elements, connecting the arbitrary states $|n_1 l_1 m_1\rangle$ and $|n_1 \tilde{l}_1 \tilde{m}_1\rangle$, of the equivalent operator

$$\frac{1}{2(Z-1)} \left[\frac{3(\mathbf{r}_1 \mathbf{A}_2)^2}{r_1^5} - \frac{\mathbf{A}_2^2}{r_1^3} - \frac{\mathbf{l}_1 \mathbf{l}_2}{r_1^3} \right]. \qquad (A.3)$$

2. Let us consider the symmetric traceless second-rank tensor $r_{2i} r_{2j} - r_2^2 \delta_{ij}/3$, where the r_{2i} are the components of the vector $\mathbf{r}_2$. From the vector integrals of motion $\mathbf{l}_2$ and $\mathbf{A}_2$ we can (with allowance for the parity) construct two similar tensors, some linear combination of which constitutes the equivalent operator for the tensor of interest to us. Let us find the coefficients of this linear combination by computing those reduced matrix elements of the tensor which connect the states $|n_2 l_2 m_2\rangle$ with the same values of l_2, as well as those with l_2 values that differ by two. The final result has the form of the operator identity

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$$r_{2i}r_{2j} - \frac{1}{3}r_2^2\delta_{ij} = \frac{5}{4Z^2}n_2^2(A_{2i}A_{2j}+A_{2j}A_{2i}-{}^2/_3A_2^2\delta_{ij})$$

$$- \frac{1}{4Z^2}n_2^2(l_{2i}l_{2j}+l_{2j}l_{2i}-{}^2/_3l_2^2\delta_{ij}). \tag{A.4}$$

which is valid within the n_2 layer. This relation is derived in another form (for the operator $x_2^2 + y_2^2$) in Ref. 10.

Let us give for reference the expression for the matrix element of the operator A_2l_1, an expression which is useful in computations:

$$\langle l_1 l_2 L; n_2 | A_2 l_1 | l_1 l_2+1L; n_2 \rangle = \frac{1}{2}\left\{ \frac{[(L+l_1+1)^2-(l_2+1)^2][(l_2+1)^2-(L-l_1)^2][n_2^2-(l_2+1)^2]}{4(l_2+1)^2-1} \right\}^{1/2}. \tag{A.5}$$

3. To allow for the contribution of the region of penetration of the outer electron to the nucleus (the k th multipole), we must compute radial matrix elements of the form

$$\int_0^\infty r_1^2\, dr_1 \int_{r_1}^\infty r_2^2\, dr_2 R_{n_1 l_1}(r_1)R_{n_2 l_2}(r_2)$$

$$\times \left(\frac{r_1^k}{r_2^{k+1}} - \frac{r_2^k}{r_1^{k+1}} \right) R_{n_1 l_1'}(r_1)R_{n_2 l_2'}(r_2)$$

(the expression for the angular integrals can be found in Ref. 7). Here we should set $l_1 = l_1'$, since the quantum number l_1 is assumed to be a "good" quantum number in our calculation. Since the unperturbed functions are superpositions of states with different l_2, we must compute the matrix elements with $l_2 \neq l_2'$.

To compute the quantum defects, we used the asymptotic expression for the function $R_{n_1 l_1}(r_1)$ for $n_1 \to \infty$ ($r_1 \ll n_1^2$):

$$R_{n_1 l_1}(r_1) = \frac{(Z-1)}{n_1^{3/2}}\left(\frac{2}{r_1} \right)^{1/2} J_{2l_1+1}\{[8(Z-1)r_1]^{1/2}\}.$$

For the Coulomb functions of the inner electron we used the explicit expressions

$$R_{n_2 l_2}(r_2) = r_2^{l_2}\exp(-Zr_2/n_2)P_{n_2 l_2}(r_2),$$

where $P_{n_2 l_2}(r_2)$ is a well-known[14] polynomial of degree $n_2 - l_2 - 1$. Owing to the properties of the angular integrals, the condition $l_2 + l_2' \geqslant k$ is fulfilled, so that the r_2 integral contains only positive powers of r_2, for which the integral can be explicitly evaluated. The subsequent integration over r_1 can be carried out analytically (the result can be expressed in terms of the Bessel functions of imaginary argument). But the direct numerical integration turned out to be simpler.

[1]Notice also that, in the numerator of the expression (10), the term $3l_1 l_2$ is small compared to the remaining terms, and makes to $U_{d2}^{(1)}$ a contribution of the order of L^{-4}. Therefore, this term is discarded in the formula (12), as well as in the calculations in Sec. 4, which are carried out up to the terms of the order of L^{-3} inclusively.

[2]The octupole term in (1) in first order perturbation theory, as well as the dipole term in third order, makes no contribution, a fact which follows from parity arguments.

[3]The formulas (14)–(17) differ from those obtained by Nikitin,[7] although they have similar structures. Having in mind application to not too large L values, we did not carry out a formal expansion in $L \to \infty$ in them.

[4]In this respect the correction is like an exchange correction. This circumstance allowed Nikitin[7] to call it an exchange-type correction.

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