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ELEMENTARY PARTICLE PHYSICS AND FIELD THEORY

CALCULATION OF THE ENERGY OF EXCITED STATES WITH ZERO ELECTRON ORBITAL ANGULAR MOMENTA

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Within the framework of the variational method, as the result of a numerical calculation we have found the energy of the excited state and the screening constant of the helium atom in the electron configuration 1s 2s, which is metastable with respect to the single-photon transition to the $1s^2$ state, and also in the 1s 3s configuration. The results of numerical calculation of the energy are in approximate agreement with other values given for these states in the literature which are available to us. For the first time, numerical calculations have also been carried out for 1s ns configurations in the range of values n = 4, ..., 9, in which the corresponding values of the energy E_n and the screening constant σ_n were obtained. It was found, in particular, that σ_n and $|E_n|$ for the excited states in the range n = 2, 3, ..., 9 fall monotonically with increasing n, where $\sigma_n \to 0$ in the formal limit $n \to \infty$, and E_n tends to the energy of a hydrogenlike atom with nuclear charge (2e), as it should be in accordance with the physical meaning of these quantities. The results of the calculations are illustrated graphically. The present study has important methodological significance in terms of the development and application of the basic principles of quantum mechanics to the helium atom.

Keywords: helium, energy, screening constant.

INTRODUCTION

An approximate theoretical calculation of the energy of helium can be carried out numerically or, in some cases, analytically using the Hylleraas variational method [1, 2], which for the ground state $1s^2$ gives results that essentially coincide with experiment (for example, see [3, 4]).In this calculation, including the first excited state $1s2s$ which is metastable with respect to the single-photon transition $(2e)^* \to (2e) + \gamma$, we use general expressions for the energy and screening constant of a two-electron atom obtained in [5] in a simple version of the variational method with one variational parameter (the atomic number Z). The given calculational method enables us, in particular, to elucidate the dependence of the energy E_n and the screening constant σ_n of the helium atom on the value of the quantum number n in the states $\{n' = 1\}$, $\{n = 2, 3, ...; l = 0\}$. The literature on calculation of the energy of the helium atom is quite extensive (for example, see [6–8] and the references cited therein); in this regard, a version of the variational method that is generally considered to be more exact, having a larger than usual [3, 4] number of variational parameters, was employed in [8]. Such an approach is supposed to deliver correspondingly more accurate calculations; however, for states with $l = 0$ only the values $n = 2$ and 3 were considered, whereas in the present study E_n and σ_n were

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calculated for $n = 2, 3, ..., 9$, where the results for E_n obtained for $n > 3$ are original to this work, and the screening constant was never calculated before.

In the present study, we are interested in the particular case of the usual three-dimensional $(D = 3)$ two-electron atom. Here the value of the energy for *energy* quantum numbers n and n' is given by an expression following from the general formulas presented in [5], including also *the spatial dimensionalities* $D = 1$ and 2, in the derivation of which, results presented in [9] were used:

$$E = -\mathrm{T}_E\,(Z - \sigma)^2, \tag{1}$$

$$\sigma \equiv \sigma^{(\pm)} = \frac{\tilde{K} \pm \tilde{J}}{\tilde{\mathrm{T}}_E}. \tag{1a}$$

The factor T_E is proportional to the summed average kinetic energy of the electrons and is equal to $\mathrm{T}_E = \left(|E_n| + |E_{n'}|\right)/Z^2$ (in this regard, see [9]), regardless of the specific values of the quantum numbers n and n' of the electrons and with the value of the total energy of each electron in the field of the nucleus (Ze) equal to

$$E_n = -\frac{(Z\alpha)^2 m_e c^2}{2n^2}, \quad \alpha = \frac{e^2}{\hbar c} \approx \frac{1}{137}. \tag{2}$$

Thus,

$$\mathrm{T}_E = \left(\frac{1}{n'^2} + \frac{1}{n^2}\right)\frac{\alpha^2 m_e c^2}{2}. \tag{2a}$$

The parameter σ in general takes into account the influence of the interaction of the electrons on the energy of the atom, and for $n' < n$ it can be interpreted as a screening constant of the field of the nucleus by the *inner electron* with quantum number n' as seen by the *outer electron* with quantum number n. The parameter $\tilde{\mathrm{T}}_E$ figuring in expression (1a) is equal to $\tilde{\mathrm{T}}_E = \left(\frac{1}{n'^2} + \frac{1}{n^2}\right)$.

If the *inner* electron is found in a state characterized by the set of quantum numbers $\{n' = 1,\, l' = 0,\, m' = 0\}$ and the *outer* electron is found in a state with the set of quantum numbers $\{n > n',\, l = 0,\, m = 0\}$, i.e., with zero orbital angular momenta, then the *quintuple* integrals in the general formulas of [5] reduce to *double* integrals $\tilde{K} \to \tilde{K}_n$, $\tilde{J} \to \tilde{J}_n$:

$$\tilde{K}_n = \left(\frac{2}{n}\right)^3 \int_0^\infty d\,\rho\,\rho\,F_n^2(x_n)\,e^{-(2/n)\rho} \int_0^\infty d\,\rho'\,\rho'\,e^{-2\rho'}\,(\rho + \rho' - |\rho - \rho'|), \tag{3a}$$

$$\tilde{J}_n = \left(\frac{2}{n}\right)^3 \int_0^\infty d\,\rho\,\rho\,F_n(x_n)\,e^{-(1+1/n)\rho} \int_0^\infty d\,\rho'\,\rho'\,F_n(x'_n)\,e^{-(1+1/n)\rho'}\,(\rho + \rho' - |\rho - \rho'|), \tag{3b}$$

analogous to what was demonstrated in [5] for the ground state with electron quantum numbers $n = n' = 1$ in a two-electron atom, where, for brevity, we denote the degenerate finite hypergeometric series thus [3, 10]:

$$F_n(x) \equiv F(-n+1,2;x)\,,\; x_n = \frac{2\rho}{n}\,,\; x_n' = \frac{2\rho'}{n}\,, \tag{3c}$$

$$F(a,b;x) = 1 + \frac{a}{b}\frac{x}{1!} + \frac{a(a+1)}{b(b+1)}\frac{x^2}{2!} + \ldots + \frac{a(a+1)\ldots(a+k)}{b(b+1)\ldots(b+k)}\frac{x^{k+1}}{(k+1)!} + \ldots\,, \tag{3d}$$

where this series for integer nonpositive a, as obtains in formulas (3c): $a = -(n-1)$, in fact truncates at the value $k = |a| - 1$.

Next, we employ the following representation of $F_n(x)$ (formula (3c)), following from formula (3d) and suitable for the numerical calculations to be performed in this work:

$$F_n(x) = 1 + \sum_{k=0}^{n-2} \frac{\prod_{j=0}^{k}(-n+1+j)}{\prod_{j=0}^{k}(2+j)} \frac{x^{k+1}}{(k+1)!}\,. \tag{3e}$$

The considered states of the atom with electron configuration $1s\ ns$ are metastable with respect to the single-photon transition $(2e)^* \to (2e) + \gamma$ to the ground state $1s^2$ since the *outer* electron, as was noted above, is effectively found in the field of the nucleus and the *inner* electron. In this case, the situation is similar to that of a one-electron atom, and therefore the single-photon transition with $\Delta l = 0$ in the case under consideration is suppressed by the corresponding selection rule *for l*, according to which $\Delta l = \pm 1$ [4]. In this situation, only the much less probable two-photon transition is allowed (for example, see [11]). The $1s2s$ state, considered below, is also *absolutely metastable* since the allowed single-photon transition is completely absent in this case.

CALCULATION OF THE ENERGY OF THE ATOM IN THE CONFIGURATIONS 1*s ns* (*n* = 2, 3, …, 9)

For the excited state $n = 2$, taking formulas (3c) and (3d) into account, it is convenient to represent expressions (3a) and (3b) in explicit form:

$$\tilde{K}_2 = \int_0^\infty d\rho\,\rho\left(1 - \frac{\rho}{2}\right)^2 e^{-\rho} \int_0^\infty d\rho'\,\rho'\,e^{-2\rho'}\,(\rho + \rho' - |\rho - \rho'|)\,, \tag{4a}$$

$$\tilde{J}_2 = \int_0^\infty d\rho\,\rho\left(1 - \frac{\rho}{2}\right) e^{-(3/2)\rho} \int_0^\infty d\rho'\,\rho'\left(1 - \frac{\rho'}{2}\right) e^{-(3/2)\rho'}\,(\rho + \rho' - |\rho - \rho'|)\,. \tag{4b}$$

These integrals, in contrast to the results for $n > 2$, are quite easily calculated, in fact analytically. Their values, calculated numerically based on general formulas (3a) and (3b), using formulas (3c) and (3d), coincided with the results obtained analytically. Results of numerical calculation of quantities (3a), (3b), (1) and (1a) for $n = 2, 3, \ldots, 9$ are displayed in Table 1 ($\sigma^{(\pm)} \to \sigma_n^{(\pm)}$, $E \to E_n^{(\pm)}$, and the quantities $|E_n^{(+)}|$ and $|E_n^{(-)}|$ are given in eV).

In an approximation for $n = 2$ that is sufficient for our purposes, based on the results of this numerical calculation, the screening constant is equal to (the *upper* number is the term ${}^1S_0$, and the *lower* number is the term ${}^3S_1$)

TABLE 1

n	2	3	4	5	6	7	8	9
$\tilde{K}_n$	0.210178	0.099409	0.057611	0.037507	0.026338	0.019502	0.015019	0.011907
$\tilde{J}_n$	0.02191	0.00576	0.00233	0.00117	0.00067	0.00042	0.00028	0.0002
$\sigma_n^{(+)}$	0.18567	0.09466	0.05642	0.03719	0.02628	0.01952	0.01506	0.01195
$\sigma_n^{(-)}$	0.15061	0.08428	0.05203	0.03494	0.02497	0.0187	0.01451	0.01157
$\left\lvert E_n^{(+)}\right\rvert$	55.9603	54.8584	54.585	54.4917	54.4516	54.4310	54.4209	54.4152
$\left\lvert E_n^{(-)}\right\rvert$	58.144	55.458	54.832	54616	54.523	54.477	54.451	54.436

$$\sigma \to \sigma_2^{(\pm)} \approx \left\{\begin{matrix} 0.19 \\ \\ 0.15 \end{matrix}\right\}, \tag{5}$$

and the absolute value of the energy is equal to

$$\left\lvert E_2^{(\pm)}\right\rvert \approx \left\{\begin{matrix} 55.96 \\ \\ 58.14 \end{matrix}\right\}. \tag{6}$$

As can be seen from the table, the values $\sigma_n^{(\pm)}$ with growth of n in the interval 3–9 fall monotonically from tenths to hundredths, and in the formal limit $n \to \infty$, they fall to zero, which corresponds to the disappearance in this case of an interaction between the electrons and, consequently, as was noted above, to the screening effect. The values of $\left\lvert E_n^{(\pm)}\right\rvert$ in the interval of values of n from 2 to 9 also decrease monotonically since the negative contribution to the total energy $E_n^{(\pm)}$ of the atom from the energy of the *outer* electron in the field of the nucleus decreases, as is clear from formulas (1) and (2a). In the formal limit $n \to \infty$, $\sigma_n^{(\pm)} \to 0$ and in the case under consideration $n' = 1$, $Z = 2$ we find that $E_n^{(\pm)} \to -\frac{(2\alpha)^2}{2} m_e c^2 \approx -54.4$ eV, i.e., it tends to the energy of a hydrogenlike atom with $Z = 2$, as it should be, and is in agreement with the numerical calculation presented in the table. These tabulated values for $\sigma_n^{(\pm)}$ and $\left\lvert E_n^{(\pm)}\right\rvert$ are presented graphically in Figs. 1 and 2 for greater clarity, where to illustrate the above-indicated asymptotic limit, the graph of $\sigma_n^{(\pm)}$ in Fig. 1 is also constructed for values of $n > 9$, which are absent in the table.

It is also worth mentioning that, as is clear from the table and from Fig. 1, $\sigma_n^{(-)} < \sigma_n^{(+)}$ for all n in the range 2–9 and, correspondingly, the energy levels of the ${}^3S_1$ terms for the same value of n are located below the levels of the ${}^1S_0$ terms in this range (2–9). This is in agreement with the results of [8] for the cases $n = 2$ and 3. Note that the

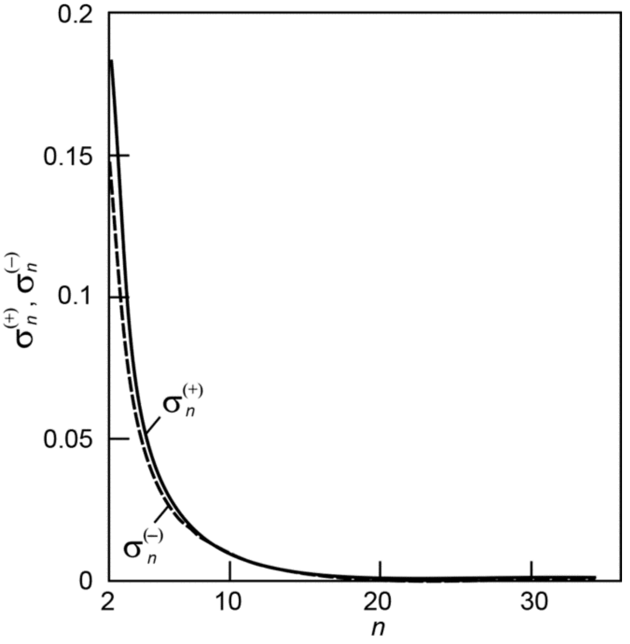

Fig. 1

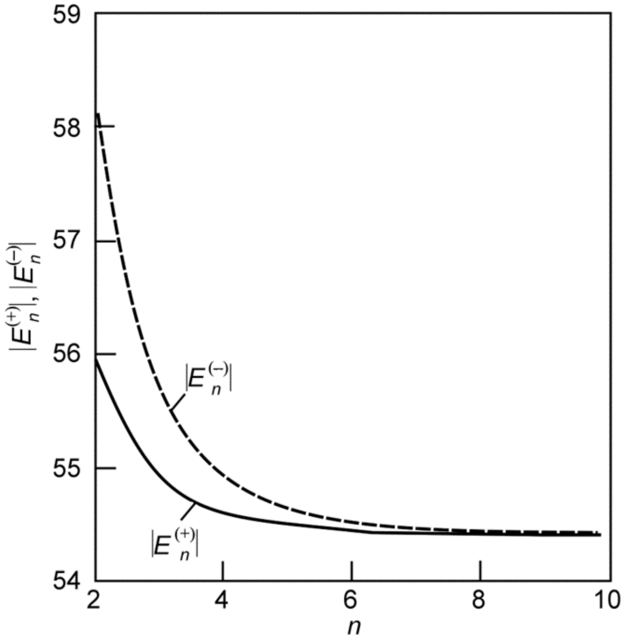

Fig. 2

Fig. 1. Dependence of the screening constant $\sigma_n^{(\pm)}$ on the principal quantum number *n* of the *outer* electron in excited states of the helium atom.

Fig. 2. Dependence of the absolute value of the energy $\left|E_n^{(\pm)}\right|$ on the principal quantum number of the *outer* electron in the lower excited states of the helium atom.

decrease in $\sigma_n^{(\pm)}$ on the interval from 2 to 3 of the graph is completely analogous to the same effect on the interval of values of n from 1 to 2 for a one-dimensional helium atom, as follows from [12], and in this case the expression for the energy (formula (2)) of a hydrogenlike atom (Ze) is the same as in the three-dimensional version [13].

The values of the energy $E_2^{(\pm)} \to E_{2RB}^{(\pm)}$ for $n = 2$, found from [14] with allowance for the ground state energy ≈ -78.90 eV given in [3, 4], are such that the relative deviations $\delta^{(\pm)} \equiv \left|E_{RB}^{(\pm)} - E_{VAR}^{(\pm)}\right| / \left|E_{RB}^{(\pm)}\right|$ of the reference values from the values obtained in our simple version of the variational method for $n = 2$, expressed as percents, are equal to $\delta_2^{(\pm)} \approx \begin{Bmatrix} 4 \\ 2 \end{Bmatrix} \%$. In the state with $n = 3$ the deviation of the energy values presented in the table from the earlier calculated values [8] and the reference values presented in [14] is equal to $\delta_3^{(\pm)} \approx \begin{Bmatrix} 2 \\ 1 \end{Bmatrix} \%$, i.e., it is roughly two times smaller. For the ground state of the helium atom, to which only the integral $\tilde{K}_1$ (formula (3a)) contributes, the deviation δ of the *variational* value from experiment amounts to $\delta \approx 2\%$, but this result, as is generally considered to be the case [3, 4], confirms the adequacy of the variational method in analytical calculations of the ground state energy. Thus, this very conclusion can be considered to be valid also with respect to our method of calculation of the energy.

Note also that if we convert the energy values given in [8] into electron-volts, then in the states 2^1S_0 and 2^3S_1 they are equal to ≈ -58.39 and -59.26 eV, respectively, with the accuracy applicable in the present study, with a deviation equal to $\delta \approx (0.2-0.3)\,\%$ from the values found from the data in [14]. This means that there are quite weighty grounds to assume that the results of [8], obtained by an *improved* variational method, more closely correspond to the real situation than our results, obtained in its simplest version.

Note that for the excited states under consideration in the above-indicated sense of metastable states, the energy of the atom found from perturbation theory, E_{pert}, can be found as the sum of energies (formula (2)) of the atomic electrons in the field of the nucleus $E_1 + E_n < 0$ and the interaction energy of the electrons $E_{\text{int}}{}^{(\pm)} > 0$, similar to how this was done in [3, 4] for the ground state (see also formula (2) of [5]). For $n = 2$ and $Z = 2$ the result of the calculation is as follows:

$$E_{\text{pert}}{}^{(\pm)} \approx -\begin{Bmatrix} 55.38 \\ \\ 57.77 \end{Bmatrix} \text{ eV}. \tag{7}$$

As can be seen, in the case under consideration there is no significant difference between these values and the more accurate result (formulas (6)) obtained by the variational method, as is also the case in the calculation of the ground state [3, 4]. Thus, in both cases the variational method and perturbation theory, with allowance for their approximate character, give almost the same result, despite the formal inapplicability of the method of perturbations; this, in a sense, can have a random character.

CONCLUSIONS

Among the main results of this study, we may highlight both the elucidation of the applicability of the simplest variational method and the method of perturbation theory to a calculation of the energy of the first excited (metastable) state $1s2s$ of the helium atom and also a numerical calculation of the energy by the variational method in the states $1s\,ns$, $n = 2, 3, \ldots, 9$ with an elucidation of the monotonic decrease of the screening constant with increasing n in this interval and all the way up to $n = 35$ (Fig. 1). It also turned out that the absolute value of the energy $\left|E_n{}^{(\pm)}\right|$ of the helium atom in the excited states for the S-terms and the quantum numbers of the *outer electron* in the interval 2–9 also decreases monotonically (Fig. 2), bearing in mind that results are presented in [8, 14] only for the energies for $n = 2$ and 3, and calculation of the screening constant is completely absent. Practically complete agreement between the results of calculations by both methods in the case $n = 2$ can be considered as an additional argument in favor of the adequacy of our approach to the problem in comparison with the results of [8], which also, like our results, differ from the reference values. The theoretical values of the energy in both studies with allowance for the fundamentally approximate character of the calculations made in them can be viewed as satisfactory in the context of their correspondence with the reference values [14].

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REFERENCES

1. E. A. Hylleraas, Z. Phys., **63**, 291 (1930).
2. E. A. Hylleraas, Z. Phys., **63**, 771 (1930).
3. L. D. Landau and E. M. Lifshitz, Quantum Mechanics: Non-Relativistic Theory, Pergamon Press, Oxford (1977).

4. A. A. Sokolov, Yu. M. Loskutov, and I. M. Ternov, Quantum Mechanics, Holt, Rinehart and Winston, New York (1966).
5. V. V. Skobelev, Russ. Phys. J. **62**, No. 2, 199 (2019).
6. R. P. Madden and K. Codling, Phys. Rev. Lett., **10**, No. 12, 516 (1963).
7. J. W. Cooper, V. Fano, and F. Prats, Phys. Rev. Lett., **10**, No. 12, 518 (1963).
8. D. T. Aznabaev *et al*., Pis'ma Fiz. Elem. Chast. At. Yad., **12**, No. 5, 1066 (2015).
9. V. V. Skobelev, Russ. Phys. J. **61**, No. 12, 2155 (2018).
10. I. S. Gradshteyn and I. M. Ryzhik, Table of Integrals, Series, and Products, Academic Press, Cambridge, MA (2000).
11. V. V. Skobelev, Russ. Phys. J., **59**, No. 10, 1623 (2016).
12. V. V. Skobelev, Zh. Eksp. Teor. Fiz, **153**, No. 3, 401 (2018).
13. R. London, Amer. J. Phys., **27**, 649 (1959).
14. A. A. Radtsig and B. M. Smirnov, Parameters of Atoms and Atomic Ions [in Russian], Energoatomizdat, Moscow (1986).