

A simple formula for ground state energy of a two-electron atom

M. Auzinsh, R. Damburg
Dept. of Physics, University of Latvia
19. Rainis blvd., Riga LV-1586, Latvia
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A simple expression for a ground state energy for a two-electron atom is derived. For this assumption based upon the Niels Bohr "old" quantum mechanics idea about electron correlation in a two-electron atom is exploited. Results are compared with experimental data and theoretical results based on a variation approach.

I. INTRODUCTION

The helium problem played an important role in the early history of quantum mechanics [1]. Already at the very beginning of "old" quantum theory Niels Bohr made his first attempt to calculate energy levels of the He atom. He discussed a model when both electrons of a two-electron atom move along the same circular orbit and are located at the opposite ends of a diameter [2]. Even some time before Bohr's attempt Hantaro Nagaoka in Japan demonstrated from the view point of classical mechanics that such motion possesses the lowest possible energy and – what is very important – it is a mechanically stable arrangement [3]. It means that weak disturbances cannot destroy this motion.

Afterwards Bohr's approach to the problem was considered to be unsuccessful mainly due to the reason that this model fails to explain diamagnetism of a two-electron atom in its lowest energy state and also the value of the obtained energy was in a rather poor agreement with experiment. Later it was assumed that only quantum mechanics can satisfactorily explain such a two-electron atom.

In this paper we will try to demonstrate, that if we combine quantum mechanical approach to the two-electron atom with ideas that were at the heart of Bohr's approach, we can obtain a very simple expression for the lowest energy level of a two-electron atom that can nevertheless describe these energies with the same accuracy as do more complicated approaches based on the quantum variation method combined with a quantum perturbation theory.

II. SCHROEDINGER EQUATION FOR A TWO-ELECTRON ATOM WITH STRONG ELECTRON CORRELATION

Let us consider a two-electron atom with a nuclear charge Z . In atomic units the stationary Schroedinger equation for this system is

$$\left(-\frac{1}{2}\Delta_1 - \frac{1}{2}\Delta_2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}\right)\psi = E\psi. \quad (2.1)$$

It is well known that to solve this equation, it is important to account correctly for electron correlation. Now let us assume, as it was done by Niels Bohr, that electrons are permanently located exactly on the opposite sides of nucleus, so that $\mathbf{r}_1 = -\mathbf{r}_2$ (a being positive). In opposition to the general case of the Schroedinger equation for a two-electron atom, with this last assumption, equation (2.1) can be solved precisely analytically. For eigenvalues the solution is

$$E_n(a, Z) = -\frac{(1+a)^2}{2n^2(1+a^2)} \left(Z - \frac{a}{(1+a)^2}\right)^2, \quad (2.2)$$

where n is a principal quantum number. This solution is not quantized in a strict sense. The energy of the atomic state depends on the particular value of the parameter a which can vary continuously. It is reasonable to look for those a values for which energy approaches its lowest value at a fixed nuclear charge Z and quantum number n . This analysis leads us to the value for $a = 1$ and we immediately arrive at the solution obtained by Niels Bohr in the "old" quantum theory, namely $E_1(1, 1) = -9/16 = -0.5625$ a.u. for the H negative ion and $E_1(1, 2) = -49/16 = -3.0625$ a.u. for He. These numerical results predict much lower ground state energies for these two-electron atoms, than it is experimentally observed, see Table 1. For this a simple qualitative explanation can be found. Above, we considered a case when a exactly equals 1 – or, in other words – electrons are constantly and exactly on the opposite ends of a diameter of a circular orbit. Obviously for the low lying states of atoms this assumption contradicts the uncertainty principle. If we take uncertainty relations into account it means that we can not say that we can permanently know

the exact location of one electron with respect to another one. As a result one can not assure that both electrons occupy all the time this most favourable from the view-point of energy spatial configuration and, as a result, the actual energy level is raised in comparison with this most favourable classical state.

III. GROUND STATE ENERGY LEVELS OF A TWO-ELECTRON ATOM – SIMPLE EXPRESSION

For a single electron atom the general solution of the Schroedinger equation is $E_n^{(s)}(Z) = Z^2 / (2n^2)$ we can express ionization energy for the two-electron atom in our model as

$$I(a, Z) = -\frac{(1+a)^2}{2(1+a^2)} \left(Z - \frac{a}{(1+a)^2} \right)^2 - \frac{Z^2}{2}. \quad (3.1)$$

Now in the framework of this model we can analyze what is the smallest nuclear charge Z_0 for which stable two electron negative ion will still exist. Moreover, for this numerical exercise, let us now let Z vary continuously and let us analyze the most favourable – with lowest energy – configuration when $a = 1$. The threshold value of Z at which ionization energy $I(a, Z)$ approaches zero and consequently one electron can be ejected from the atom, which means that the Helium-like ion ceases to exist is

$$Z_0 = \frac{1}{2} + \sqrt{\frac{1}{8}} \approx 0.85355. \quad (3.2)$$

It can be interpreted in a sense that at $Z = Z_0$ only those hypothetical negative ions for which both electrons are *all the time exactly* on the opposite ends of the diameter of a circular orbit ($a \equiv 1$) can survive. This means that in this limit of small Z values the expression

$$E_1(a = 1, Z \propto 1) = -(Z - 1/4)^2 \quad (3.3)$$

can be a good approximation for the energy levels for this very fragile hypothetical Helium like ion. We realize very well that the last analysis is only a numerical exercise performed with Eq. (3.1) and in a real world there do not exist ions with fractional nuclear charge Z , but, on the other hand, we will show further, that the obtained ground state energy expression (3.3) can be successfully used as asymptotic approximation for ions with small integer Z values.

Probably, such a hypothetical ion with $Z_0 \approx 0.85355$ if it existed could not survive for very long before autoionization, because, as it was mentioned above, the assumption about permanent location of the electrons at opposite ends of the diameter contradicts the uncertainty principle.

On the other hand it is known that the variational principle with only one variational parameter – the effective nuclear charge – can lead to the expression for energy in the form [4]

$$E_1^{(v)}(Z) = -\left(Z - \frac{5}{16} \right)^2. \quad (3.4)$$

This formula is known to give rather good agreement with experiment at the opposite limit when $Z \gg 1$. This fact, namely that formula (3.4) is good at the limit of large Z values, can be easily understood.

The classical text book problem is to calculate the energy states of a two-electron atom by means of perturbation theory. At the very beginning one can easily solve the problem neglecting electron – electron interaction (problem of independent electrons) and then one can consider electron – electron interaction as a perturbation. Obviously, this approach will not be very good for small Z values, when nucleus – electron interaction and electron – electron interaction is of the same magnitude. But if Z is getting larger and larger, approximation is getting better and better, since nucleus – electron interaction is getting strictly predominant. In the first order the perturbation theory gives for energy [4]

$$E_1^{(p)}(Z \gg 1) = -Z^2 + \frac{5}{8}Z \quad (3.5)$$

which in a large Z limit coincides exactly with (3.4).

Let us now combine the expression for small Z values – Eq. (3.3) and that for large Z values – Eq. (3.4) into one. Such an expression can be constructed in a rather simple form

$$E_1(a, Z) = -\left(Z - \frac{1 + \frac{1}{4}\sqrt{1 - Z_0/Z}}{4} \right)^2. \quad (3.6)$$

The energies given by this expression can be compared with ground state energies obtained for a two-electron atom with nuclear charge Z . The first method for calculating these energies was worked out by Hylleraas [5]. The method was based on a variation approach combined with perturbation theory. If function with 50 summands was used as a probe function Hylleraas obtained after laborious calculations ground state energy dependence on Z for a two-electron atom in the form [6]

$$E_1^{(H)}(Z) = -Z^2 + \frac{5}{8}Z - 0.157652 + O\left(\frac{1}{Z}\right). \quad (3.7)$$

Finally, the quality of both Z energy dependences must be compared with experimental results for two electron atoms. The best experimental values for these energies for wide range of ions can be found in the National Institute of Standards data base [7].

IV. DISCUSSION

Today advanced numerical calculations of two electron atoms are available. For the classical example of the ground state of a helium atom the nonrelativistic energy of the ground state is obtained with an accuracy of one part in 10^{19} . For this a basis set containing 2114 terms was used, see [8] and references therein.

Despite these spectacular achievements it is still interesting, in our opinion, to analyze a simple and easy understandable approach to helium-like atoms. The experimental values of ground state energies for He-like atoms, together with energies given by expressions Eq. (3.6) and (3.7) are collected in Table 1. In the third column of this table experimental values of ground state energies of He-type atoms are given. The fourth column contains the energies for the same ions calculated from Eq. (3.6), as derived in this work. The fifth column of Table 1 contains energy values calculated from the Hylleraas expression (3.7) obtained by means of a variational approach combined with the perturbation theory. Energies from both expressions agree relatively well with each other for all Z values, and with experimental data for small Z . For larger Z formulae yield larger energies (less negative) than those measured in experiment. This difference is due to relativistic and QED corrections that are not included in these formulas. During the years relativistic and QED corrections have been measured and calculated many times with increasing accuracy, see for example [9]. Nevertheless, for our purpose, when we do not expect spectroscopic accuracy for the simple formulae under discussion, an estimate of these effects can be used to account for them. For an arbitrary two-electron atom the relativistic correction to the ground state energy can be calculated as [4]

$$E_{rel} = -\frac{1}{8}\alpha^2 Z^2 (Z^2 - 3.606Z + 3.29 + 0.05Z^{-1}) \quad (4.1)$$

In a similar way the QED correction for ground state energy can be found as [4]

$$E_{QED} = \frac{16Z^4\alpha^3}{6\pi} [(3.745 - \ln Z) - Z^{-1}(5.97 - 1.31 \ln Z) + Z^{-2}(3.08 - 0.28 \ln Z)] \quad (4.2)$$

These corrections must be added to the ground state energy values obtained from expressions Eq. (3.6) and Eq. (3.7). If we now compare the corrected ground state energies obtained with experimental values, agreement is very good. In Figure 1 the relative differences $(E_e - E_t)/E_e$ between theoretical energy E_t calculated from the respective formulae (3.6) or (3.7), together with corrections (4.1) and (4.2), and experimental energy E_e are presented. We can see that in most cases the relative difference is less and in most cases significantly less than 0.1%. An exception is the energy from the Hylleraas formula for the negative H ion. These discrepancies can not be, at least not significantly, reduced if we take into consideration the finite mass of the nucleus. An account for this can lead to the relative increase of the ground state energy in comparison of the value obtained from (3.7) for about m/M where m is a mass of the electron, but M is the mass of the nucleus [4]. Apart from this simple effect of the finite mass of the nucleus upon the energy levels of the ion, there exist secondary – usually smaller – effects connected with correlation in electron motion [4]. Nevertheless, it is known that correlation effects in electron motion for a two-electron atom in quantum mechanics are insignificantly small for ground state S energy levels, and this correction for ground state energy can be neglected.

Account for finite nucleus mass in Bohr's model when both electrons are constantly located at the opposite ends of a diameter of a circular orbit can differ from usual conclusions about the atomic S state. In this model the motion of both electrons is obviously strongly correlated. It must strongly decrease the influence of nuclear motion upon the

calculated ground state energy, if not cancel it totally. In the case, when both electrons are all the time on a circular orbit on opposite ends of a diameter, the nucleus will remain at rest all the time in laboratory coordinates.

In the overall, approximation given by Eq. (3.6), which was obtained practically without any adjustable parameters agrees with experiment better than the Hylleraas formula. Maybe this can be considered only as a curious coincidence, but we think that this expression for ground state energy of a two-electron atom may be of some interest. As a starting point for the derivation of the energy for a He-like atom ground state the approach of old Bohr's quantum mechanics was used. This approach in some textbooks still is viable for achieving intuitive understanding of a theory of atomic structure.

One may ask why the square root $\sqrt{1 - Z_0/Z}$ was chosen in formula (3.6). Any other power of p in the expression $(1 - Z_0/Z)^p$ would give the same asymptotic behaviour of the energy for small as well as for large Z values. The actual power $p = 1/2$ was chosen on the ground of the best coincidence with experimental results, combined with the willingness to obtain a simple final expression. Actually, the best coincidence with experimental results can be obtained at p value slightly larger than $1/2$ (around 0.56). One must realize, that an exact value of a parameter p , at which the best coincidence between experiment and expression (3.6) can be obtained, varies slightly for different Z values. Nevertheless, it is surprising how close it remains to 0.56 in a broad range of Z values. Taking into account all this and the obvious circumstance, that one can not expect very high accuracy from such a simple expression as (3.6) which is not based on very sound assumptions, and trying to derive a simple expression we have chosen $p = 1/2$ in a final expression.

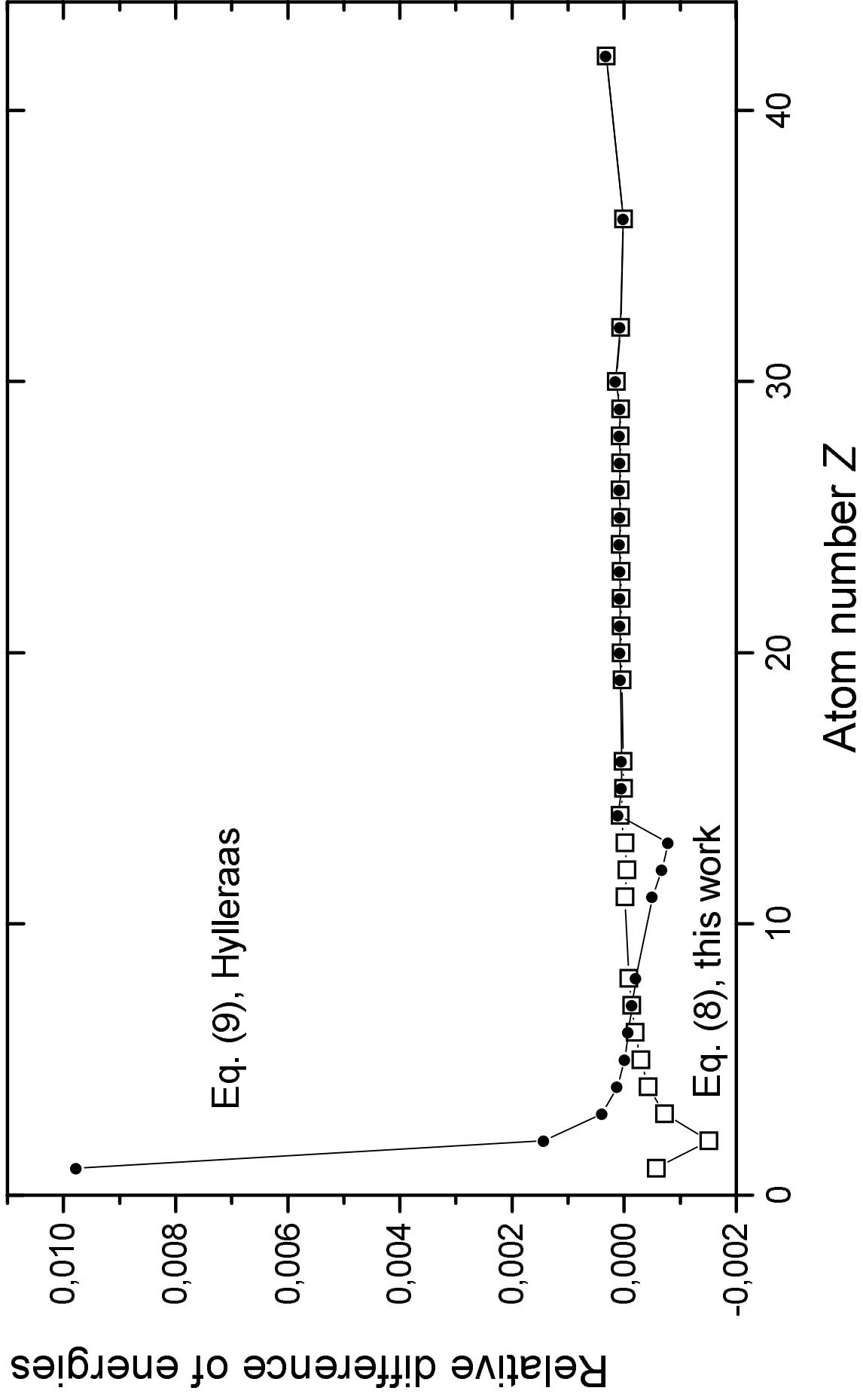
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TABLE CAPTION

Table 1. Experimental values of the ground state energies for a He-like atoms [7], the energies obtained from Eq. (3.6) and Eq. (3.7) together with the relativistic and QED corrections to these energies. Energy is given in atomic units.

FIGURE CAPTION

Figure 1. The relative differences between the corrected ground state energies for a He-type atoms calculated from Eq. (3.6) (squares) and Eq. (3.7) (*circles*) and experimental values for these energies.



Z	Ion	Experiment	Eq. (8)	Eq.(9)	Relativistic correction	QED correction
1	H(1-)	-0,5275	-0,5272	-0,5327	0,0000	0,0000
2	He	-2,9035	-2,8991	-2,9077	0,0000	0,0000
3	Li(1+)	-7,2798	-7,2745	-7,2827	-0,0001	0,0000
4	Be(2+)	-13,6560	-13,6498	-13,6577	-0,0005	0,0001
5	Be(3+)	-22,0330	-22,0250	-22,0327	-0,0017	0,0003
6	C(4+)	-32,4100	-32,4002	-32,4077	-0,0042	0,0006
7	N(5+)	-44,7890	-44,7753	-44,7827	-0,0088	0,0011
8	O(6+)	-59,1700	-59,1504	-59,1577	-0,0164	0,0018
11	Na(9+)	-114,3400	-114,2755	-114,2827	-0,0682	0,0054
12	Mg(10+)	-136,7500	-136,6506	-136,6577	-0,0997	0,0072
13	Al(11+)	-161,1600	-161,0256	-161,0327	-0,1411	0,0094
14	Si(12+)	-187,5812	-187,4006	-187,4077	-0,1941	0,0006
15	P(13+)	-216,0196	-215,7757	-215,7827	-0,2609	0,0148
16	Si(14+)	-246,4716	-246,1507	-246,1577	-0,3435	0,0181
19	K(17+)	-349,9419	-349,2757	-349,2827	-0,7107	0,0299
20	Ca(18+)	-388,4774	-387,6507	-387,6577	-0,8818	0,0344
21	Sc(19+)	-429,0435	-428,0258	-428,0327	-1,0819	0,0392
22	Ti(20+)	-471,6439	-470,4008	-470,4077	-1,3143	0,0441
23	V(21+)	-516,2785	-514,7758	-514,7827	-1,5823	0,0492
24	Cr(22+)	-562,9475	-561,1508	-561,1577	-1,8892	0,0542
25	Mn(23+)	-611,6690	-609,5258	-609,5327	-2,2388	0,0592
26	Fe(24+)	-662,4247	-659,9008	-659,9077	-2,6348	0,0640
27	Co(25+)	-715,2421	-712,2758	-712,2827	-3,0810	0,0685
28	Ni(26+)	-770,1029	-766,6508	-766,6577	-3,5817	0,0726
29	Cu(27+)	-827,0347	-823,0258	-823,0327	-4,1410	0,0762
30	Zn(28+)	-886,0363	-881,4008	-881,4077	-4,7633	0,0006
32	Ge(30+)	-1010,2228	-1004,1508	-1004,1577	-6,2157	0,0818
36	Kr(34+)	-1283,6589	-1273,6509	-1273,6577	-10,0887	0,0707
42	Mo(40+)	-1756,3279	-1737,9009	-1737,9077	-18,9731	-0,0175