

A Strong Contradiction in the Conventional Non-relativistic Theory of the Ground State Helium Atom and Helium-like Ions

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Abstract In the conventional theory of the ground state of helium atom, any solution of the two-electron Schrödinger equation is wrong! That is caused by a strong imbalance of proportions of the attraction versus repulsion operators' acting on a wave function, in the initial differential Schrödinger equation and in its integral algebraic form. In the differential equation, the attraction operators act on the radial part of wave function independently from one another obeying the true proportion: one attraction versus one repulsion per electron. But the resulting wave function turns out to satisfy the wrong integral proportion: two attraction energies versus one repulsion energy per electron. The underlying contradiction is un-coincidence of the additivity rules of energies and energy operators: whereas energies of the electrons may be summed the corresponding energy operators referred to different electrons may not. Consequences of this principal contradiction are discussed.

Keywords Schrödinger Equation, Attraction/Repulsion Operators, Integration

1. Introduction

Helium atom is the simplest many-electron system. Its theory should be a benchmark of correct approximate description of the electron-electron and electron-nucleus interactions. Agree to common viewpoint the physical grounds of the theory are known exactly and the only problem of interest is a high precision of calculations[1, 2]. Charles Schwartz writes[3]: "For thousands of years mathematicians have enjoyed competing with one another to compute ever more digits of the number π . Among modern physicists, a close analogy is computation of the ground state energy of the Helium atom, begun 75 years ago by E. A. Hylleraas". Up to date, the total energy is computed with up to 42 decimal digits[4].

In reality, the state of the art of the helium atom problem is not so brilliant at all. In this relation it is important to underline that solution of a Schrödinger equation, first of all, must yield a correct wave function describing just the system under study. We found that the conventional theory of helium atom, invented in 20-30th of the last century contains a substantial contradiction which prevents obtaining the true solution. That contradiction is contradiction between the rules of summing energy operators and energy components. We can and may sum energies of particles. Those are just

numbers. But we may not sum attraction energy operators related to different particles. This principal contradiction leads to many other contradictions and pseudo quantum mechanical misconceptions of the theory. First of them is the next: while the initial Schrödinger equation is formally correct any algebraic equation obtained from it by integration yields substantially wrong radial part of wave function.

Section 2 is devoted to a brief description of the conventional theory. In Section 3, the conventional theory is revised. It is demonstrated that 1) integration of the two-electron Schrödinger equation strongly violates true initial proportion of attraction and repulsion operators per electron acting on wave function and 2) Schrödinger equation for one of electrons is free of such a fundamental shortcoming. Corresponding total and orbital energy calculation errors (so named correlation energies) are compared. Section 4 shows an example of advantage of the proposed approach in treating relation between atomic sizes and interatomic distances.

2. Basic Features of the Conventional Non-relativistic Theory of Two-electron Atoms

Traditionally, the ground-state wave function and energy of helium atom and its isoelectronic ions are obtained by solving the two-electron non-relativistic stationary Schrödinger equation[5– 7]:

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$$\left(-\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}\right)\Psi(\mathbf{r}_1, \mathbf{r}_2) = E\Psi(\mathbf{r}_1, \mathbf{r}_2). \quad (1)$$

In Eq. (1), \mathbf{r}_i are the position vectors of electrons, r_1 and r_2 stand for distances from the first and second electrons to the infinitely heavy nucleus of charge Z which is placed in the center of coordinates, r_{12} is distance between the electrons. E is energy of the two electrons. Conventionally, this is so called total energy which is equal to the sum of the sequential ionization energies (or potentials IP) of the first and second electrons, $E = E_1 + E_2 = -(IP_1 + IP_2) < 0$. Spin coordinates in wave function and corresponding interaction operators in Hamiltonian are excluded for the sake of simplicity. Here and further atomic units $m_e = e = \hbar = 1$ are used.

Since the Eq. (1) can not be solved analytically exactly[5–10] an approximate or numerically exact solution is sought as expansion in a series under necessary condition

of the total energy minimization:

$$(\int \Psi^* H \Psi) / (\int \Psi^* \Psi) \rightarrow \min = E. \quad (2)$$

Thus the two-electron physical problem is reduced to mathematical problem of convergence of the series to produce the deepest energy minimum. Great efforts were done in developing the Hylleraas-type calculations[9–14] where Ψ depends on r_{12} explicitly. The Hylleraas method provides the highest accuracy of energy computation considerably exceeding experimental one[1, 4, 14]. Alternative are configuration interaction method[15] or its combination with Hylleraas method[16], Hartree-Fock and perturbation theory methods[17–19]. These methods would be very efficient if the procedure of solving the equations (1) and (2) were correct. In the next section we shall show that the procedure contains a substantial and insoluble contradiction.

3. The Contradiction between the Differential and Integral Forms of Eq. (1)

3.1. General

Let us take the wave function in a very general form (in spherical coordinates) $\Psi = \Psi(r_1, \theta_1, \varphi_1, r_2, \theta_2, \varphi_2)$ and assume it be an exact parameter-free or a very accurate variation solution of Eq. (2). Then we have:

$$\begin{aligned} (\int \Psi^* H \Psi) / (\int \Psi^* \Psi) = & -\frac{1}{2} \int \Psi^* (\nabla_1^2 + \nabla_2^2) \Psi / (\int \Psi^* \Psi) - (\int \Psi^* (\frac{Z}{r_1} + \frac{Z}{r_2}) \Psi) / (\int \Psi^* \Psi) \\ & + (\int \Psi^* \frac{1}{r_{12}} \Psi) / (\int \Psi^* \Psi) = 2K + 2P_{attr} + P_{rep} = E \end{aligned} \quad (3)$$

where K , P_{attr} and P_{rep} are positive kinetic, negative attraction and positive repulsion energies, respectively. The attraction energy is radial one, by definition. When compare Eq. (1) with Eq. (3) it is seen a substantial difference. First, in the initial Eq. (1) the attraction energy operators Z/r_1 and Z/r_2 act on the radial part of the wave function independently in agreement with the basic postulate of theory: electrons attract to nucleus independently from one another. In counteraction with the operators of kinetic and repulsion energies, the attraction operators create certain curvature of radial part of electronic wave function and, hence, certain mean (expectation) value of radial distance for each of the electrons. They cannot assist one another in creating the curvature and the mean radial distance. Second, there is definite proportion between the attraction and repulsion energy operators. It is the next one: one attraction operator and one repulsion operator per electron. This is just so because the repulsion operator should act on wave function in the same fashion as repulsion does: it acts on both electrons at any instant of time. Just this rule is read in Eq. (1). There the attraction operators depend on distances r_1 and r_2 whereas the repulsion operator depends on distance r_{12} , that is, on both r_1 and r_2 .

The Eq. (3) contradicts to these rules strongly. There the two identical attraction energies are summed with no reference to definite electron whereas repulsion energy remains ordinary. That proportion is substantially different from the initial proportion of attraction/repulsion operators per electron and considerably increases the curvature of the radial part of sought wave function. As a consequence, to solve Eq. (1) by any method becomes senseless. For any wave function, the obtained minimum lies deeper of the sum of real energies of electrons. Below it will be demonstrated on the examples of explicit functions.

3.2. Kellner Function

In order to expose the insoluble contradiction most clearly let us choose the simplest Kellner's orthonormal variational radial wave function[8]:

$$\Psi(r_1, r_2) = \psi_1(r_1)\psi_2(r_2) = (k^3 / \pi) e^{-k(r_1 + r_2)}. \quad (4)$$

Note that this type of function is correct in principle because a priori it is known that both electrons in a helium atom occupy the same spherically symmetrical 1s state with opposite spins. It is important to note that the function depends not only on variable coordinates but on the variation parameter k as well. Function (4) corresponds to the so named case of independent electrons. Shortcoming of the function is well known: under integration the expectation value of energy is obtained by summing interactions of all elementary volumes of space. Therefore, the function allows the electrons meeting each other at very small distances and even at the same point. Commenting on representation of a two-electron wave function in the form of a single anti-symmetric product of wave functions of the electrons Taylor and Parr[15] noticed that “such wave functions ... allow the electrons to move independently of one another; hence, in general, the functions are not small, as they should be, when the electrons are close together. One says that the wave function does not correlate the motion of the electrons, and the difference between the correct ground-state energy of a system and that calculated with the best function of this type (the Hartree-Fock function) is called the correlation energy.” In fact, this function leads to too strong repulsion which in turn leads to insufficiently deep total energy minimum. On the other hand, the advantage of the function is that it reduces the two-electron problem to one-electron (hydrogen-atom) one and parameter k has meaning of screened nuclear charge Z_{eff} and mean momentum p .

For the present study, just first two properties are important, the independence of electronic functions ψ_1 and ψ_2 and the too strong repulsion. It is important to see that in the Eq. (1) the attraction operator Z/r_1 acts only on function $\psi_1(r_1, k)$ and operator Z/r_2 acts only on function $\psi_2(r_2, k)$ of wave function (4). The operators create certain curvature of radial electronic wave functions ψ_1 and ψ_2 expressed by a value of the variation parameter k . Since the electrons are identical the value of k is the same for both electrons. We would like to underline that the attraction operators act independently on independent functions ψ_1 and ψ_2 , respectively. Therefore, they create definite curvatures of these functions in agree with the proportion ‘one attraction versus one repulsion’. It would exclude any doubling of attraction under integration if it were not fatally un-avoiding. Below we shall show that it is not so.

The value of the parameter k is found from Eq. (2). For function (4), corresponding algebraic equation is the next:

$$k^2 - 2Zk + \frac{5}{8}k = E. \quad (5)$$

It is seen that the Eq. (5) comprises sum of the two kinetic, two attraction and one repulsion, energies, like Eq. (3). Yet these are not just numbers until k is calculated. These are integral operators acting directly on the value of the variation parameter. However, the proportion of the attraction/repulsion operators per electron is already 2/1, instead of 1/1 in Eq. (1). In the Eq. (5), the operators act on k jointly or sequentially as if the second of the operators acts on the wave

function which was already modified by first one. Resulting value k_{\min} :

$$k_{\min} = Z_{\text{eff}} = (Z - \frac{5}{16}) \quad (6)$$

of the variation parameter of wave function (4) in the total energy minimum:

$$E_{\text{theor}} = -(Z - \frac{5}{16})^2 \quad (7)$$

is too big. It characterizes *each of the electrons* as attracting to nucleus with double force and repelling the counter electron with ordinary force. This is absurd. Electrons cannot assist each other in attracting to nucleus. It is easy to understand that this absurd situation is caused by the integration operation. Integration wipes out coordinates of electrons and, hence, very important information about the independent action of attraction operators on the independent radial functions of electrons.

Thus the function (4) represents most striking example of incorrectness of obtaining the expectation value of energy from Eq. (1). It would be clear that a correct procedure is summing only operators referred to one electron like summing force vectors in classical mechanics. Therefore it is necessary to solve the stationary Schrödinger equation for one of interacting electrons:

$$(-\frac{1}{2}\nabla_1^2 - \frac{Z}{r_1} + \frac{1}{r_{12}})\Psi(\mathbf{r}_1, \mathbf{r}_2) = E_1\Psi(\mathbf{r}_1, \mathbf{r}_2), \quad (8)$$

where E_1 is orbital energy of each electron. Eq. (8) is free of the doubling effect of summing attraction energy operators. Respective algebraic equation is the next one:

$$\frac{k^2}{2} - Zk + \frac{5}{8}k = E_1. \quad (9)$$

This equation satisfies the proportion “one attraction versus one repulsion” presumed in the initial Eq. (1). It yields value of k_{\min} :

$$k_{\min} = Z - \frac{5}{8}. \quad (10)$$

One can readily find that the value obtained from Eq. (5) is arithmetic mean of this and of that of helium ion He^+ : $(Z - 5/16) = [(Z - 5/8) + Z]/2$. From this it follows that the wave function (4) derived from Eq. (1) describes an artificial system intermediate between helium atom and helium ion. That abstractive kind of system does not have any interest for physics because it does not follow the true laws of physics.

Then two important questions appear: 1) is it possible and sufficient to solve the Eq. (8) and 2) is not the function (4) appropriate to properly describe the stationary state including correlation of electrons? In this relation it is important to note that the energy minimum:

$$E_1^{\text{theor}} = -(Z - \frac{5}{8})^2 / 2 \quad (11)$$

turns out to lie deeper (!) than the experimental one (for helium, $-0.9453 < -0.9037$) in contrast to the case of total

energy minimum: $-2.8477 > -2.9037$ (Table 1). In Table 1, the symbol of an element in the column headings is accompanied with the number of the equation, from which the corresponding values are obtained; $\langle r \rangle = 1.5/k$ is the mean radial distance from nucleus to every of the electrons. We would underline that the deep E_1^{theor} minimum appears in spite of the strongest repulsion got in the model of independent electrons! Therefore, correlation of electrons tending the electrons to be farther from one another is not a major effect ignored if use function (4). That unknown phenomenon has another nature. Further we shall show that it is the classical property of inertia of electrons which is missed in the conventional theory.

3.3. Eckart Function

The described strong violation under integration of the initial true balance of attraction/repulsion operators leading to a too much high value of k is not specific feature of just the wave function (4). The same result is got if use Eckart-type function:

$$\Psi(r_1, r_2) = N(e^{-k_1 r_1 - k_2 r_2} + e^{-k_1 r_2 - k_2 r_1}). \quad (12)$$

This function differs from the function (4) only by explicit symmetry relative to permutation or exchange of unobserved states characterized by parameters k_1 and k_2 which comprise the observable k state. In this case, arithmetic mean of k_1 and k_2 is also equal to $(Z - 5/16)$. More important is to point out that the exchange does not favour lowering the system energy. It is easily seen from comparison of the energy values $[(k_1 + k_2)/2]^2$ and $(k_1^2 + k_2^2)/2$. For example, the values of the parameters in helium atom wave function equal to 1.19 and 2.184, respectively. Then we have the inequality: $-2.848 > -3.093$. Therefore, the exchange consumes energy, in complete agreement with the laws of classical mechanics.

In relation to function (12) it is suitable to give physically meaningful dynamical interpretation of the roots of Eq. (9). The equation has two different roots $k_1 \neq k_2$ (Table 1). Agree to Viète's formulas, $(k_1 + k_2)/2 = (Z - 5/8)$ and $k_1 k_2/2 = -E_1$. Hence, the minimum of the left-hand side of (9) corresponds to arithmetic mean of the roots while the true energy value equals half of their product. This contradiction is resolved if assume that the inter-electronic repulsion perturbation splits the stationary k -state into a couple of unobservable temporary states 1 and 2. The sought stationary k -state is formed by averaging in time the temporary states. The roots k_1 and k_2 have physical meaning of average momenta p_1 and p_2 and effective nuclear charges of the electrons in the corresponding temporary states 1 and 2. Furthermore, it is important that the arithmetic mean of the roots would represent a momentum p of the time-averaged stationary state of each of the electrons if they occupied their virtual states with equal probability or during equal time intervals. It is worth noting that the Eckart-type function (12) describes just that kind of situation. It implies that electron 1 occupies state 1 when electron 2 is in state 2 thus screening each other. But it is evident, that in state 1, each of the electrons has a smaller momentum and occupies a larger volume. Therefore,

both the electrons spend *more time* in this state than in the state 2. This asymmetry results in a decrease of the mean kinetic energy of the stationary state which is characterized by parameters $Z_{\text{eff}} = p = k = (k_1 k_2)^{1/2} = (-2E_1)^{1/2}$. The effect can be interpreted in terms of classical physics, as inertia of the electron motion. Electronic interaction takes form of alternate "hydrogen-like" movements of the electrons from the centre (acceleration) to periphery (deceleration) and vice versa.

3.4. Mean Radial Distance in Highly Precise Hylleraas-type Calculations

To treat the Hylleraas-type functions is excessive because those explicitly depend on inter-electronic distance r_{12} and evidently make sure that the electrons never occupy the same point in the space and tend to be far from one another. Therefore, this kind of function tends to make repulsion between the electrons weaker. Therefore, it tends to strengthen attraction. But the mistake found in the present study is just too much strong attraction owing to the physically senseless summing (doubling) of the attraction operators, after integration! Then irrespective to the number of variation parameters and variables, any wave function produced by Eq. (1) describes an artificial system intermediate between proper helium atom and He^+ ion. It does not describe the helium atom.

Nonetheless, there is an interesting property of Hylleraas-type functions that would be advantageous in calculations. Lowering energy by means of enlarging the mean $\langle r_{12} \rangle$ distance by those functions is followed by corresponding increase of mean radial distance $\langle r \rangle$ and, consequently, of volume of the atom. For example, expectation values of radial distance in helium atom and negative hydrogen ion equal 0.929 and 2.710, respectively [1]. These values are larger than those calculated from Eq. (5): 0.880 and 2.065. That is, this kind of function increases the volume and lowers energy of the atom. However, these mean distances are substantially smaller than those calculated from Eq. (9): 1.1157 and 6.3667, respectively. The difference of the radii, in picometers, is enormous, especially in view of the X-ray diffraction measurement precision (0.1-0.01 pm): 9.88 and 193.50, respectively. It makes impossible to compare interatomic distances in molecules and condensed matter with atomic radii. In Section 4, we shall demonstrate one of examples of strong advantage of the present radii.

3.5. Inertial Nature of the Correlation Energy ΔE_1

The correlation energies, that is, calculation errors ΔE_1 and ΔE are defined here as differences between the experimental or exact values of mean total or orbital energies and those theoretical:

$$\begin{aligned} \Delta E_1 &= E_1^{\text{exact}} - E_1^{\text{theor}} \\ \Delta E &= E^{\text{theor}} - E^{\text{exact}} \end{aligned} \quad (13)$$

where E_1^{theor} and E^{theor} are calculated in formulas (11) and (7), respectively. In terms of the roots of Eq. (9) and Eq. (5) the correlation energies are equal $\Delta E_1 = (k_2 - k_1)^2/8$ and $\Delta E = (k_2 - k_1)^2/4$, respectively. It can be seen from Table 1. Precision of the exact total energy values retrieved from literature[1, 4, 11] is restricted by five decimals (Table 2). In the paper[20], we noticed that the values of the correlation energies slightly vary in helium-like atoms. In the present study, we proceed exploring this phenomenon. In Figure 1, we have plotted the energy error ΔE_1 against inverse nuclear charge ($1/Z$), $Z = 1-12$. For the set of ions from Mg^{10+} to B^{3+} , this dependence is approximated by a straight line:

$$\Delta E_1^{\text{lin}} = 0.00835/Z + 0.03767, \quad (14)$$

with a high precision. Linear dependence (14) is certainly true because relative strength of the repulsion perturbation is inversely proportional to nuclear charge. The dependence has correct extrapolation behaviour at $Z \rightarrow \infty$ that is at the hydrogen-like atom limit where the perturbation is absent. In contrast to the considered dependence the total energy error:

$$\Delta E^{\text{lin}} = -0.00833/Z + 0.05998 \quad (15)$$

has an untrustworthy behaviour. This error increases with Z increasing. It contradicts to relative weakening of repulsion perturbation in ions with high nuclear charge and thus serves as an additional confirmation of correctness of the orbital-energy consideration of the helium atom problem.

From Figure 1 it is seen that the correlation energy ΔE_1 is positive for all the elements under study. As mentioned in Section 3.2, this means that in spite of overestimation of the repulsion energy with function (4), the $P_{\text{rep}}/P_{\text{attr}}$ ratio is not a major source of correlation energy. To shift the orbital energy minimum higher it is necessary to decrease Z_{eff} that is to expand atom. That is accompanied by decreasing mean kinetic energy and lifting up potential energy. Since K depends on Z_{eff} stronger than P_{attr} (Eq. (9)) then just this energy should be considered as a main source of the orbital energy error though the virial relation holds, of course. Since Eq. (8) (with function (4)) is radial then the only physical cause of decreasing kinetic energy is inertia of radial component of electron motion, namely the process of accelerating of electrons from a turning point at periphery to the centre. In this relation it is worth noting that the constant in Eq. (14) would really represent inertial part of hydrogen-like atom's energy. Electron in a hydrogen atom also obeys the law of inertia. Neither Eq. (1) nor Eq. (8) account for the phenomenon of inertia because they are stationary and deal only with probability of electrons to be at some points. Inertia is property of classical particles and requires time-resolved consideration of quantum electron motion. Feynman's formulation of quantum mechanics seems to be most suitable tool to solve this problem because the peaks of electron wave packets are known to move classically. This kind of problem is a challenge for theorists. Note that the hydrogen-atom problem does not require special time-dependent treatment because exactly known charge of the nucleus provides exact determination of potential and, hence, kinetic energies. As for helium atom,

the author is aware of the only one study treating the problem in terms of Feynman path integrals[21]. However, there the traditional total energy calculations are done.

Now it is necessary to determine contribution of the repulsion energy error to correlation energy ΔE_1 . For that purpose, let us return to Figure 1. For lighter elements, ΔE_1 values are smaller than Eq. (14) predicts, with the largest deviation:

$$\Delta_1 = \Delta E_1^{\text{lin}} - \Delta E_1 \quad (16)$$

in negative hydrogen ion. Just this deviation reveals the error of calculation, with use of the function (4), of the mean electron repulsion energy or the ratio $P_{\text{rep}}/P_{\text{attr}} = 5/8$. A correct minimum of orbital energy satisfying Eq. (14) is the next one:

$$E_1^{\text{lin}} = -(Z - x)^2 / 2. \quad (17)$$

The values of x :

$$x = \frac{ZP_{\text{rep}}}{P_{\text{attr}}} = \frac{\langle r_{12}^{-1} \rangle}{\langle r^{-1} \rangle} \approx \text{const} \times \frac{\langle r \rangle}{\langle r_{12} \rangle} \quad (18)$$

are presented in Table 2. It is important that the increment Δ_1 is positive. It means that taking into account the repulsion energy error leads to an increase of that of orbital energy. It is caused by opposite acting of inertia and the observed variation of $x = \langle r_{12}^{-1} \rangle / \langle r^{-1} \rangle$ ratio on the size of atom: the former tends to expand atom and the latter tends to compress it.

On the other hand, the variation of x ratio obeys the following rules. First, while highly charged positive ions have it precisely equal to 0.625, in the sequence Be^{2+} , Li^+ , He and H^- it lowers down to 0.616. Thus, 0.625 is the uppermost limit of the ratio. That is evident because repulsion is strongest in the independent electron model presented by function (4). Second, the range of its variation is narrow and its values are close to 0.625. This law would be expected when an isoelectronic series is considered. Moreover, it would be considered as a substantial quantum mechanical property of two-electron atoms. Even in very large negative hydrogen ion the ratio is far from the value 0.5, in the case of classical circle orbit, where $\langle r_{12}^{-1} \rangle / \langle r^{-1} \rangle = \langle r \rangle / \langle r_{12} \rangle$. These values should be compared with those obtained in Hylleraas-type high precision calculations. Agree to the data in Table 11.6 of handbook[1] the ratio equals 0.5941, 0.5832, 0.5602 и 0.4552, within the mentioned sequence. The latter number is smaller than the classical limit! Third, the ratio notably varies only in relatively large atoms (ions). It points out on volume $V_A = 4.5\pi (-2E_1)^{-3/2}$ as the most relevant atomic property that directly relates to the probability of the electrons to meet one another and would govern the $\langle r_{12}^{-1} \rangle / \langle r^{-1} \rangle$ or $\langle r \rangle / \langle r_{12} \rangle$ ratios. The second one is mean kinetic energy K . Both properties are determined by curvature of wave function of the atom and, in turn, by its effective nuclear charge. If consider atomic electrons as some localized objects, corpuscles or wave packets, then it is clear that probability P_c of the electrons to occur to be close

to one another is inversely proportional to the atomic volume (Table 2). The dependence $P_c \sim 1/V_A$ is not known. The author would only suppose that it has a dynamic origin. The probability of the electron-projectile and electron-target to avoid a collision depends on their momenta because the electrons can not change those in an instant of time. Thus the cause is inertia again. The rule reads: the higher velocity of electrons the higher probability P_c . In large negative hydrogen ion, V_A is very big and K is very small. It leads to much lesser P_c and corresponding larger repulsion energy error than in small helium atom and positive ions (Table 2, Figure 1). In H^- ion, the repulsion energy error comprises one eighth of the electron energy whereas the inertial one is

twice the energy itself.

Concluding this Section, it should be underlined that the proposed inertial nature of correlation energy implies a time-resolved consideration of the helium atom problem. It means that electrons tend to move on definite trajectories and be at the same point in space at different instants of time. Square of function (4) represents time-averaged distribution of electron density and all interactions are expressed by value of the parameter of exponents of the function. As such, the function (4) is sufficient to correctly describe the stationary ground state of helium atom. The problem is how to determine the true value of the parameter.

Table 1. The screened charges, energies and mean radii of the helium atom and some isoelectronic ions

Parameter	H^- (5)	H^- (9)	He (5)	He (9)
k_1	$0.6875 - i0.2347$	0.0826	$1.6875 - i0.2368$	1.0860
k_2	$0.6875 + i0.2347$	0.6674	$1.6875 + i0.2368$	1.6640
$(k_1 + k_2)/2$ E, E_I	0.6875 -0.4727	0.3750 -0.0703	1.6875 -2.8477	1.3750 -0.9453
$(k_1 k_2)^{1/2}$ E, E_I	0.7265 -0.5277	0.2356 -0.0277	1.7040 -2.9037	1.3444 -0.9037
$\langle r \rangle$	2.0647	6.3667	0.8803	1.1157
	Li^+ (5)	Li^+ (9)	Be^{2+} (5)	Be^{2+} (9)
k_1	$2.6875 - i0.2393$	2.0900	$3.6875 - i0.2406$	3.0932
k_2	$2.6875 + i0.2393$	2.6600	$3.6875 + i0.2406$	3.6568
$(k_1 + k_2)/2$ E, E_I	2.6875 -7.2227	2.3750 -2.8203	3.6875 -13.5977	3.3750 -5.6953
$(k_1 k_2)^{1/2}$ E, E_I	2.6981 -7.2799	2.3579 -2.7799	3.6953 -13.6556	3.3632 -5.6556
$\langle r \rangle$	0.5559	0.6361	0.4059	0.4460

Table 2. Variation of the $\langle r_{12}^{-1} \rangle / \langle r^{-1} \rangle$ ratio in helium-like atoms

Atom	$-E$	$\langle r_{12}^{-1} \rangle / \langle r^{-1} \rangle$	$1/V_A$
H^-	0.52775	0.615883	0.00387
He	2.90372	0.624814	0.71998
Li^+	7.27991	0.624977	3.88434
Be^{2+}	13.65557	0.624994	11.27161
B^{3+}	22.03097	0.625	24.65908
C^{4+}	32.40625	0.624999	45.82449
N^{5+}	44.78145	0.624999	76.54545
O^{6+}	59.15660	0.624999	118.59983
F^{7+}	75.53171	0.625	173.76537
Ne^{8+}	93.90681	0.624999	243.81976
Na^{9+}	114.28188	0.625	330.54088
Mg^{10+}	136.65694	0.625	435.70640

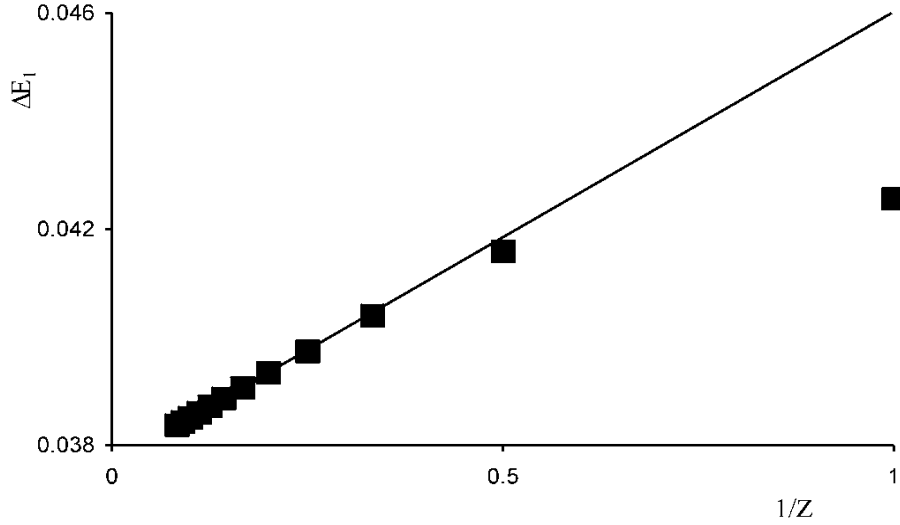


Figure 1. Dependence of the correlation energy ΔE_1 on the inverse nuclear charge, for the helium isoelectronic series. The linear trend refers to the correlation energy ΔE_1^{lin} accounting for the repulsion energy error, filled quadrangles – to ΔE_1

4. Problem of Relation between Atomic Radii, Interatomic Distances and Bond Energies: Homonuclear Diatomic Molecules of the Elements from H through Ne

The necessity of a time-resolved description of electrons' movement in a two-electron atom strongly supports an assumption of the present author on necessity of a time-resolved consideration of covalent bonding in homonuclear molecules. The idea is that electrons tend to visit the area between nuclei namely the overlap area at different time intervals[22]. Then the covalent interaction can be represented by simple overlap of spherical atoms preserving radii of isolated atoms (R_A), and dissociation energy D_0 of a homonuclear molecule is proportional to the depth of overlapping of atoms dR ($dR = 2 R_A - R$, R is the inter-nuclear distance). Both D_0 and R are known from experimental table data. A beautiful curve of the dependence D_0 (dR):

$$D_0 = 20.667e^{0.0286(dR)}. \quad (19)$$

was obtained for elements of six periods of the Mendeleev Table, with a very slight scatter of points. It is presented on Figure 2. On the curve, there are two regions, those of covalent ($dR > 0$) and Van der Waals interaction ($dR < 0$). Corresponding atomic radii are proportional to ionization potentials of atoms and decrease slowly in the direction from the left to the right in groups of the Mendeleev Table. For example, $R_{\text{Li}}/R_{\text{Ne}} = 161/100 = 1.61$. Such a behaviour is in agreement with a good sense because electronic repulsion would strongly resist to contraction of electron shells of atoms. The obtained empirical radii are comparable with the radii calculated in traditional way and confined by a definite level of electron density, except for alkali earth metals, especially for beryllium.

However, it is well known that most rigorous quantum mechanical value of atomic radius is expectation value of

radial distance of respective electron shell. Following this rule we were to revise the theory of the simplest two-electron atom system in a way like that reported above. We managed to find strong arguments in favour of the orbital approach and calculate radii of the elements of first and second periods. Radius of hydrogen atom is known exactly, radius of helium atom is calculated with a high precision. Radii of other elements at hand are calculated roughly because the state of the art of the theory does not allow achieving accurate values. As discussed above on the example of helium atom it is not clear how to minimize energy of the electrons in an atom. All what we know about wave function of outer electron in a many-electron atom is that for atoms with $Z > 2$ a ground state function must be of type intermediate between hydrogen-like $1s$ and $n l$ -functions.

We proceeded in a following way. A solution of the hydrogenic equation:

$$-(1/2)\partial^2 R / \partial r^2 - (1/r)\partial R / \partial r - (k/r)R + l(l+1)R/2r^2 = E_1 R \quad (20)$$

sought in the form of Slater-type radial function:

$$R_l(r) = N r^l e^{-kr/n} \quad (21)$$

The next relations were obtained:
orbital energy

$$E_1 = \frac{2l^2 + 3l - 4nl - 2n + 1}{2n^2(2l+1)(l+1)} k^2, \quad (22)$$

mean radius

$$\langle r \rangle = n(2l+3)/2k. \quad (23)$$

Then the values of quantum numbers n and l were taken as arithmetic means: $n = 1.5$ ($1 < n < 2$), $l = 0.5$ ($0 < l < 1$), for all elements of the second period. The value of parameter k was calculated for given experimental E_1 . Resulting values of mean atomic radii are such that the difference between the mean radii of lithium and neon atoms is considerably smaller than in the conventional calculations: $R_{\text{Li}}/R_{\text{Ne}} \approx 2$ versus 4.

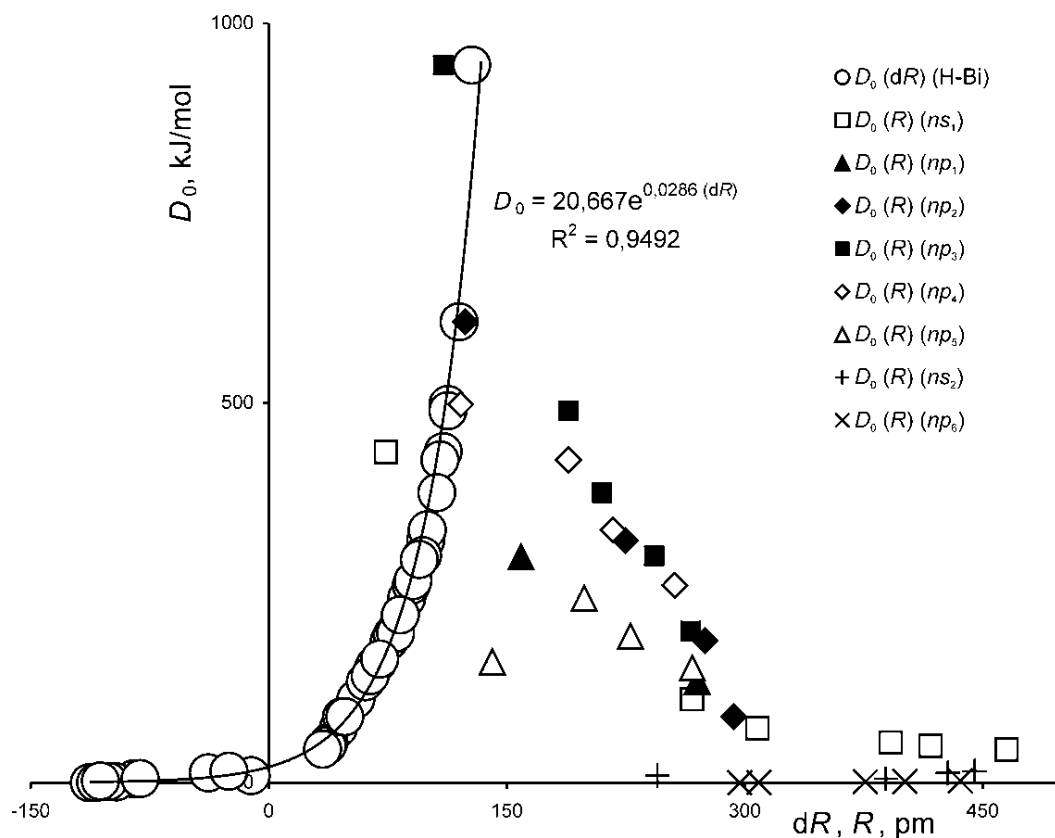


Figure 2. Empirical dependences $D_0(dR)$ and $D_0(R)$ for covalent and van der Waals homonuclear diatomic molecules[22]

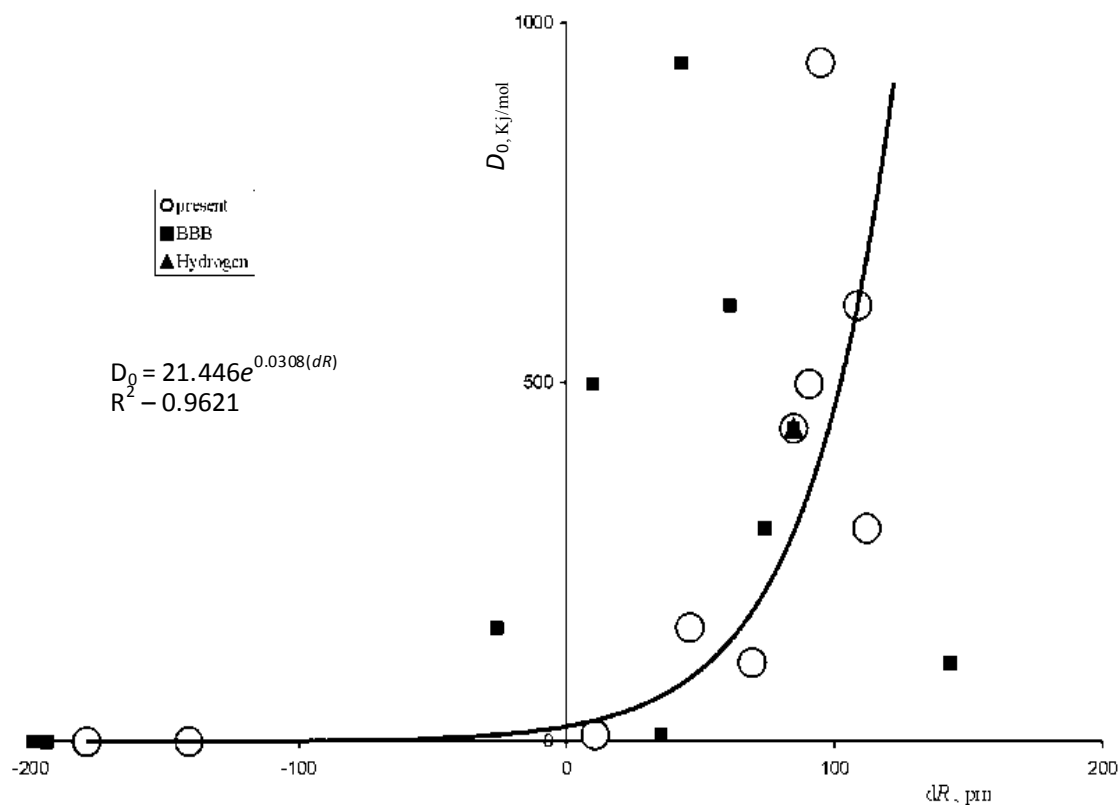


Figure 3. Theoretical dependences $D_0(dR)$ for diatomic molecules of the elements from hydrogen to neon[20]. Open circles refer to the author's calculations, filled quadrangles (BBB) – to the data of Bunge et al.[23]

Due to this reduction of the difference, a dependence of dissociation energies of diatomic molecules on the degree of overlapping of atomic orbitals becomes apparent. On Fig. 3, two dependences D_0 (dR) ($dR = 2\langle r \rangle - R$) are presented, those with use of conventional and of new radii. One can easily see a considerable difference in the scatter of corresponding points. The “new” dependence is described by the curve:

$$D_0 = 21.446e^{0.0308(dR)}, \quad (24)$$

with the parameters close to those in (19). It is important to note that a scatter of points in this type of dependence is entirely owing to the rate of mentioned above decrease of atomic radii from Li to Ne. Even more important is that this law is dictated by the experimental interatomic distances. Therefore, there are grounds to expect that real atomic radii decrease slower. In turn it means that the used procedure of calculation of atomic radii (equations 20-23) does not account for increasing repulsion or inertia of electrons in atoms of elements from Li to Ne.

5. Conclusions

On the basis of above considerations we come to conclusion that there certainly exists an insoluble contradiction in the conventional theory of the ground state of helium atom and helium-like ions. The contradiction is that between the rules of summing of energy operators and energy values of different particles. The theory allows precise calculating the value of total energy. But each of the electrons in a helium atom does not possess a half of the total energy. Their energies are equal to ionization energy. The remaining energy is that of relaxation to the helium ion state which is characterized by much deeper energy minimum and lesser volume.

More important is the wave function of the system. It should accurately correspond to true physical laws of motion of the electrons. The conventional theory ignores some of them. The central deficiency of the theory is a substantial overestimation of attraction of electrons to nucleus caused by incorrect summing the attraction operators. It is correct to sum energies of the electrons. Those are just numbers. But it is incorrect to sum the attraction energy operators related to different electrons. The Eq. (1) requires wave function satisfy to the proportion ‘one attraction versus one repulsion’ whereas the integrated one with any trial wave function requires it satisfy the proportion ‘two attractions versus one repulsion’. Owing to the incorrectness any solution of the Eq. (1) has an exceeding curvature. Moreover, it does not describe real motion of the electrons in a two-electron atom. In fact, calculating total energy is a cunning trick aiming to get solution of the two-electron atom problem through the only one stationary Schrödinger equation and entirely in terms of probability density, like the hydrogen atom problem. Unfortunately, the two-electron problem cannot be solved in such a way. It requires a time-resolved treating because

electrons can visit the same point in space at different instants of time. Therefore, trajectories of the electrons should be explored. This is not surprising for the particles possessing the rest mass. Hence, it is necessary to use Newton or Feynman mechanics. In both cases the problem of correlation, in its present form, disappears because the electrons turn out to visit the same point at different instants of time. Then the function (4) becomes very suitable stationary function describing an averaged in time distribution of electron density and all interactions.

The reported contradiction is met not only in the theory of two-electron atoms. It is principal one also in theory of many electron atoms and molecules. Therefore, to get a correct benchmark solution of the two-electron problem is very important.

In conclusion, we find reasonable to distinguish three entities that govern the ground state of a two-electron atom: 1) volume independent probability represented in the stationary Schrödinger equation by the wave function (4); 2) volume dependent probability to find electrons close to one another; it is supposed to be steered by 3) classical dynamics of electron wave packets caused by their inertial properties.

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