Shift of the 1^1S State of Helium

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In this paper the shift of the 1^1S state of helium is reconsidered and it is shown that recent discussions of the problem are subject to considerable doubt. The doubt arises from the unreliability (to the required precision) of the current theoretical determinations of the energy of the ground state. The result of an improved calculation for the latter is presented; and if this is accepted as a sufficient approximation, an unexplained shift of 21.5 cm^{-1} (opposite in direction to that previously suggested) would result for He. Similar unexplained shifts (but in the same direction as those suggested earlier) are also predicted for the other He-like ions.

A NUMBER of investigators[1] have recently tried to determine the electromagnetic shift (Lamb shift) of the ground state of He and He-like ions. Unfortunately, the experimental value for the ionization potential of He is known[2] only to ± 15 cm^{-1}, or perhaps ± 5 cm^{-1}, which is of the order of the expected shift. In preparation for a new and more precise spectroscopic determination of the ionization potential of He at Ottawa, it appeared of interest to inquire how reliable the presently accepted theoretical value of I(He) is and whether its accuracy can be improved. It is generally assumed that the energy of the ground state of helium is known from theory with an accuracy (± 2 cm^{-1}) appreciably better than from experiment. But an examination of the calculations in the literature shows that the situation is by no means so favorable.

As is well known, Hylleraas[3] made the first successful attempt to reach a high degree of accuracy in the theoretical prediction of the ground state of two-electron systems, including helium and the negative hydrogen ion. His calculations were based on the variational principle; and in minimizing the energy given by wave functions of chosen forms, Hylleraas assumed that

$$\psi = e^{-\frac{1}{2}ks} \sum c_{lmn}(k)^{l+m+n} s^l t^m u^n, \tag{1}$$

where s, t, and u are related to the distances r_1, r_2, and r_{12} (measured in atomic units) of the two electrons from the nucleus and each other, respectively, by

$$s = r_1 + r_2, \quad t = r_2 - r_1, \quad \text{and} \quad u = r_{12}. \tag{2}$$

Further in Eq. (1), k and the c_{lmn}'s are constants with respect to which the energy is minimized. By choosing a wave function of the form

$$\psi = e^{-\frac{1}{2}ks}(1 + \beta u + \gamma t^2 + \delta s + \epsilon s^2 + \zeta u^2), \tag{3}$$

with six parameters, Hylleraas[4] found for E the value

$$E(\text{helium}) = -2.90324 \text{ atomic units.} \tag{4}$$

Also it has generally been stated that "an eighth approximation" gives the improved value[5,6]

$$E(\text{helium}) = -2.903745 \text{ atomic units.} \tag{5}$$

Though this value has been widely quoted and used, it must be pointed out that it was not found by a strict application of the variational principle. The value (5) was derived by a semiempirical procedure based on an alternative method in which the energy of the ground state of a two-electron system is expressed as a series in the reciprocal of the nuclear charge Z. But this latter method cannot be relied upon to the same extent as the variational principle in that we cannot even be certain whether the calculated value is greater or less than the true value. That the value (5) should be suspect is apparent when we note that using the same method Hylleraas derived for the ground state of the negative hydrogen ion the value

$$E(H^-) = -0.52642 \text{ atomic unit,} \tag{6}$$

whereas Henrich[7] has derived the value

$$E(H^-) = -0.52756 \text{ atomic unit} \tag{7}$$

by a variational method using a wave function of the form (1) with eleven parameters.

For the reasons stated earlier, we have attempted an improved calculation of the energy of the ground state of helium by applying the variational principle to a wave function of the form

$$\psi = e^{-\frac{1}{2}ks}(1 + \beta u + \gamma t^2 + \delta s + \epsilon s^2 + \zeta u^2 + \chi_6 su + \chi_7 t^2 u + \chi_8 u^3 + \chi_9 t^2 u^2) \tag{8}$$

[1] H. A. S. Eriksson, Nature **161**, 393 (1948); M. Günther, Physica **15**, 675 (1949); H. E. V. Håkansson, Arkiv. Fysik **1**, 555 (1950); B. Edlén, Arkiv. Fysik **4**, 441 (1951).

[2] C. E. Moore [*Atomic Energy Levels*, National Bureau of Standards Circular No. 467 (Government Printing Office, Washington, D. C. 1952)] gives the old Paschen value 198305±15 cm^{-1}, while J. J. Hopfield [Astrophys. J. **72**, 133 (1930)] and B. Edlén (reference 1) gives values of 198314 and 198312±5 cm^{-1}, respectively. *Note added in proof:*—Recent measurements by R. Zbinden and one of us (G. H.) at Ottawa confirm that the last-mentioned limit of error is a very conservative one.

[3] An account of Hylleraas's investigations will be found in H. Bethe, *Handbuch der Physik* (J. Springer, Berlin, 1933), Vol. 24, No. 1, pp. 353–363, see particularly pp. 358, 362, and 363.

[4] E. A. Hylleraas, Z. Physik **54**, 347 (1929), particularly p. 358.

[5] For example, Bethe (reference 3) states that "und nach einer noch genaueren Rechnung von Hylleraas wird schliesslich in achter Näherung."

[6] E. A. Hylleraas, Z. Physik **65**, 209 (1930).

[7] L. R. Henrich, Astrophys. J. **99**, 59 (1944).

with ten parameters. [It may be noted here that the terms in u, t^2, s, s^2, u^2, su, t^2u, and u^3 are the same ones which Hylleraas used in his calculations for determining the value (5).] The results of the calculations are summarized in Table I. This table gives the coefficients β, γ, etc., for three wave functions in the range in which E takes the minimum value. The energy of the ground state given by the calculations is therefore

$$E(\text{helium}) = -2.903603 \text{ atomic units.} \tag{9}$$

We conclude that there is no basis for supposing that the ground state of helium is given by the often quoted value (5).

The value (9), like Hylleraas's values (4) and (5), represents the total energy of He assuming infinite mass of the nucleus and is based on the nonrelativistic wave equation. Hylleraas and Bethe have shown that most of the effect of the motion of the nucleus can be taken into account by using the Rydberg constant R_{He} for He rather than that for infinite mass R_∞ in converting the atomic units to cm^{-1}. A small residual correction, called mass polarization by Bethe, amounts to only 5.2 cm^{-1}.

TABLE I. The constants of a ten-parameter wave function for the ground state of helium: $\psi = \mathfrak{N}e^{-\frac{1}{2}ks}(1+\beta u+\gamma t^2+\delta s+\epsilon s^2+\zeta u^2+\chi_6 su+\chi_7 t^2u+\chi_8 u^3+\chi_9 t^2u^2)$ ($\mathfrak{N}$ is the normalization factor).

k	3.5100255	3.5299360	3.5498639
β	+0.350563	+0.352547	+0.353024
γ	+0.157394	+0.157622	+0.160254
δ	−0.129341	−0.120909	−0.112542
ϵ	+0.0130191	+0.0126717	+0.0124213
ζ	−0.0681335	−0.0708333	−0.0722356
χ_6	+0.0192383	+0.0231770	+0.0272757
χ_7	−0.0338436	−0.0322601	−0.0333144
χ_8	+0.0055753	+0.0057980	+0.0056875
χ_9	+0.0053420	+0.0051526	+0.0056020
E	−2.9036027	−2.9036022	−2.9036014
$\mathfrak{N}$	0.37984145	0.37356893	0.36764807

The relativity correction has been subject to considerable change depending on the approximation used. According to a first approximation worked out by Bethe,[3] it was estimated to be −27 cm^{-1} with Hartree functions and −10 cm^{-1} using a still simpler eigenfunction. Eriksson,[8] on the basis of higher approximations, obtains +2 cm^{-1}. These numbers are to be understood as net corrections for the energy difference between the ground states of He and He$^+$. Including the mass and relativity corrections, one finds from (9) for the ionization potential of He, the value

$$I_{\text{calc}}(\text{He}) = 198287.7 \text{ cm}^{-1}, \tag{10}$$

while the observed value[2] is

$$I_{\text{obs}}(\text{He}) = 198313 \pm 5 \text{ cm}^{-1}. \tag{11}$$

In computing (10) from (9), the Lamb shift of the ground state of He$^+$ has been neglected. If it is assumed that this shift of He$^+$ is correctly given by the Bethe-Schwinger theory, i.e., is 3.8 cm^{-1}, one obtains

$$I_{\text{calc}}(\text{He}) = 198291.5 \text{ cm}^{-1}. \tag{12}$$

TABLE II. Observed and calculated values of the ionization potentials of He-like ions.

Z	Ion	I.P.$_{\text{obs}}$, cm^{-1}	I.P.$_{\text{calc}}$, cm^{-1}	I.P.$_{\text{obs}}$ − I.P.$_{\text{calc}}$, cm^{-1}
2	He I	198313	198291.5	+21.5
3	Li II	610079	610049	+30
4	Be III	1241225	1241309	−84
5	B IV	209196$_0$	2092240	−280
6	C V	316245$_0$	3163009	−559
7	N VI	445280$_0$	4453848	−1048
8	O VII	596300$_0$	5964970	−1970

The difference between observed and calculated values is much greater than the estimated limit of error of the observed value. The question whether the difference (21.5 cm^{-1}) is due to an electromagnetic shift (opposite in direction to the Lamb shift), or to incorrect mass or relativistic corrections, or to a failure of the tenth-order approximation in approaching the correct value, must be left to future investigations. With regard to this last point, we are at the present time working on a wave function with 14 parameters.

Similar large discrepancies between observed and calculated values arise for the He-like ions. Hylleraas has derived a widely quoted general interpolation formula for the ionization potentials of these ions from the values for H$^-$, He, and a hypothetical ion with $Z=\infty$. Using the revised values for H$^-$ and He and Hylleraas's value for $Z=\infty$, one finds the following modified formula

$$\text{I.P.} = R_Z\left(Z^2 - \frac{5}{4}Z + 0.31488 - \frac{0.020896}{Z} + \frac{0.011096}{Z^2}\right).$$

The values calculated from this formula, and corrected for relativity and mass polarization effects according to Eriksson[8] as well as for the Lamb shifts of the H-like ions, are compared with the observed values as given by Edlén[1] in Table II. The observed values are larger than the calculated ones for He and Li$^+$, but smaller for the other He-like ions and increasingly so with increasing Z. The difference (last column of Table II) represents a shift of the $1s^2\,^1S$ ground state referred to the state of the bare nucleus and the two electrons at infinite distance. For Li$^+$, as for He, this shift is opposite in direction to, and appreciably larger than, the "ordinary" Lamb shift, while for the other elements it is in the same direction and about twice as large as the Lamb shift for the corresponding one-electron systems. In agreement with expectation, the shift for $Z \geq 4$ is roughly proportional to Z^4 as was already found by Edlén on the basis of the Hylleraas formula. Edlén's shifts are approximately half those of Table II, since he referred the ionization potential to the unshifted ground state of the corresponding H-like ions. It must be emphasized that for the higher He-like ions the probable error of the observed ionization potentials is a considerable fraction (about one-third) of the shift.

[8] H. A. S. Eriksson, Z. Physik 109, 762 (1938).