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Effect of the Lamb shift upon ionization potentials or excitation energies of atoms and ions

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The effect of the Lamb shift upon the ionization potential of the He-like atoms in their ground states is analyzed. It is shown that the Lamb shift of the ground state of the He-like atom tends to twice the same quantity of the H-like atom of the same Z in its ground state when $Z \to \infty$. From this observation, it is supposed that the Lamb shift of a given state of an atom or an ion with more than one electron is made up of the one-electron contributions, which can be calculated with the well known formulas for the radiative corrections to the energy levels of one-electron atoms by introducing the concept of the effective nuclear charge. To confirm this supposition, it is shown that the radiative corrections for the energy levels of the $2\ ^{1,3}S$ states of the He atom as well as for the fine structure splittings of the $2\ ^3P$ and $3\ ^3P$ states of the He atom can be understood along the same line. It is finally concluded that the effect of the Lamb shift upon the ionization potential or the excitation energy may have to be considered only if a $1s$ electron is involved either in the ionization or in the excitation.

I. INTRODUCTION

It is well known that not only the relativistic effect but also the radiative effect or the Lamb shift must be taken into account, in order to compare the nonrelativistic total energy accurately calculated for an atom with the experimental value.[1,2] Such a necessity should also arise when the nonrelativistic total energy is to be obtained from the sum of the experimental ionization potentials,[3-5] since each of the ionization potentials is subject to the radiative effect upon atomic species present before and after the ionization. It is the purpose of the present paper to show that the radiative effect upon a given energy level of a many-electron atom is made up of one-electron quantities or contribution of each of the electrons within the atom and that the one-electron contribution can be calculated at least approximately by the well known formula for the radiative correction to states of the hydrogen-like atom, through the analysis of the data on the Lamb shift of the one- and the two-electron systems. It will be shown that the radiative effect or the Lamb shift of the ionization potential or the excitation energy may have to be considered only if a $1s$ electron is involved in the ionization or excitation.

II. ANALYSIS OF THE DATA ON THE He-LIKE ATOMS IN THEIR GROUND STATES

The radiative effect on the energy levels of an atom with more than one electron has first been investigated in order to compare the ionization potential based upon very accurate nonrelativistic calculations of the He-like atoms in their ground states with the experimental values.

The Lamb shift contribution ΔI to the ionization potential of a He-like atom is

$$\Delta I = E_{L,1} - E_{L,2} - E_{L,2'}, \tag{1}$$

where $E_{L,1}$ is the Lamb shift of the ground state of the one-electron system produced by removing a $1s$ electron from the He-like atom, while $E_{L,2}$ is the Lamb shift term for the He-like atom arising from the nuclear potential and $E_{L,2'}$ is the correction arising from radiative interactions between the two electrons. Kabir and Salpeter[1] have calculated all the quantities involved in Eq. (1) and have estimated ΔI for the He-like atoms. Pekeris[2] has used this technique to show that his theoretical value of the ionization potential of the neutral He atom calculated very accurately, agrees with Herzberg's accurate experimental value[6] within the quoted experimental error. This would mean that Kabir and Salpeter's calculation on $E_{L,1}$, $E_{L,2}$, and $E_{L,2'}$ are fairly accurate. In Table I, these quantities are given for $Z = 2$, 4, and 10. It may be seen that both $E_{L,1}$ and $E_{L,2}$ increase upon increase of Z and that $E_{L,2}/E_{L,1}$ seems to approach 2 when Z increases, although it is less than 2 for lower Z values. It has therefore been decided to extend the calculation and to check the behavior of $E_{L,2}/E_{L,1}$ and $E_{L,2'}/E_{L,2}$ over a wide range of Z, i.e., $Z = 1$ through 100 000. In Fig. 1, $E_{L,2}/E_{L,1}$ and $E_{L,2'}/E_{L,2}$ are plotted against Z. It may be seen that $E_{L,2}/E_{L,1}$, starting from 1.416 for $Z = 2$ (neutral He), increases monotonically and approaches its asymptotic limit 2. As for $E_{L,2'}/E_{L,2}$, it is about -0.03 for a smaller Z value and has a singular point at around $Z = 42$: it becomes abruptly $+0.743$ for $Z = 43$ by changing the sign and decreases monotonically toward its asymptotic limit zero.

TABLE I. Numerical values of $E_{L,1}$, $E_{L,2}$, and $E_{L,2'}$ (a.u.).[a]

Z	$E_{L,1}$	$E_{L,2}$	$E_{L,2'}$
2	1.6105(− 5)	2.2805(− 5)	− 1.0188(− 6)
4	1.9915(− 4)	3.3672(− 4)	− 1.3747(− 5)
10	4.7541(− 3)	8.9061(− 3)	− 2.9260(− 4)

[a] Numbers in parentheses are the powers of ten by which the number should be multiplied.

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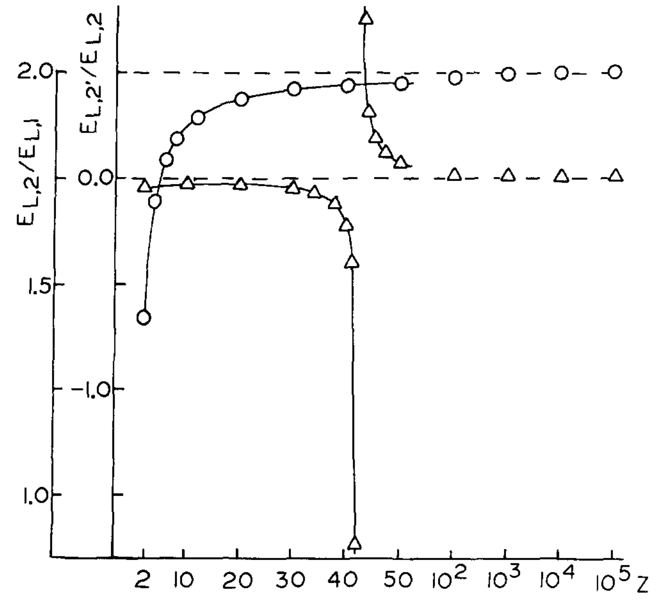

FIG. 1. Variation of $E_{L,2}/E_{L,1}$ (–O–) and $E_{L,2'}/E_{L,2}$ (–Δ–) with Z showing their asymptotic behavior.

The observation mentioned above can be explained as follows: The role of electron interaction is negligible compared with the nucleus–electron attraction, especially when Z is very large. Therefore, a quantity related to the nucleus–electron interaction of a two-electron atom is expected to be twice the same quantity of the one-electron atom of same Z if both the atoms are in the ground states. Thus, $\lim_{Z\to\infty} E_{L,2}/E_{L,1} = 2$ can be understood. The fact that $\lim_{Z\to\infty} E_{L,2'}/E_{L,2} = 0$ may also be regarded as a consequence of the relative unimportance of the electron interaction when $Z\to\infty$. From this point of view, $(E_{L,2}/2 + E_{L,2'})$ may be regarded as the contribution to the Lamb shift of a screened 1s electron. By fitting a cubic function of Z to the $E_{L,1}$ data at $Z = 1, 2, 3,$ and 4, an empirical formula has been established for the contribution of a 1s electron to the Lamb shift as a function of Z. We have then searched those Z value which reproduce the $E_{L,1}$ value identical to $(E_{L,2}/2 + E_{L,2'})$ of the neutral He atom and have found that $Z = 1.793$. This effective value of Z corresponds to the screening effect $s = 2 - 1.793 = 0.207$. Although this value of the screening effect is about two thirds of the value calculated with the Slater rules,[7] it may be regarded as the screening effect determined with reference to the Lamb shift.

From the observation mentioned above in this section, it may be concluded that the Lamb shift of a given state of a many-electron atom can be obtained as the sum of one-electron quantities, calculated by introducing the concept of the screening effect due to the other electrons.

III. EXCITED STATES OF TWO-ELECTRON ATOMS

We now test the conclusion derived in the preceding section, by applying it to the excited states of the He atom for which fairly accurate informations are available.

As mentioned in the preceding section, the basic data required for our calculation on the Lamb shift of an energy level of an atom or an ion with more than one electron is the shift $\Delta E(n,l)$ of the energy level of the hydrogen-like atom with the principal and the azimutal quantum number n and l, respectively. Formulas for $\Delta E(n,0)$ and $\Delta E(n,l)\,(l\neq 0)$ are summarized by Bethe and Salpeter[8] and may be written in hartrees as follows:

$$\Delta E(n,0) = \frac{4Z^4\alpha^3}{3\pi n^3}\left[2\log\frac{1}{Z\alpha} + \log\frac{Z^2}{K_0(n,0)} + (19/30)\right] \tag{2}$$

and

$$\Delta E(n,l) = \frac{4Z^4\alpha^3}{3\pi n^3}\left\{\log\frac{Z^2}{K_0(n,l)} + (3/8)\left[c_{lj}/(2l+1)\right]\right\}, \tag{3}$$

where

$$c_{l,j} = \begin{cases} (l+1)^{-1} & \text{for } j = l+\frac{1}{2} \\ -l^{-1} & \text{for } j = l-\frac{1}{2} \end{cases}$$

and α is the fine-structure constant. The ratio $K_0(n,l)/Z^2$ is independent of Z and varies rather slowly with n. For S states, this ratio is given to be 19.770, 16.640, 15.921, 15.640, and 15.2 for $n = 1, 2, 3, 4,$ and ∞, respectively. For $l \neq 0$, this ratio is very close to unity for all n; for P states, for example, it is given to be 0.9704 and 0.9590 for $n = 2$ and 4, respectively.[8] Before proceeding any further, it should be noted that Eqs. (2) and (3) give adequate values of $\Delta E(2,0)$ and $\Delta E(2,1)$ with $j = \frac{1}{2}$, 13 619.93 and -206.07 MHz, respectively, for $Z = 2$, amounting to the ${}^2S_{1/2}$–${}^2P_{1/2}$ separation of 13 826.00 MHz (cf. experimental value $14\,044.5 \pm 5.2$ MHz[9]).

Let us now discuss the excited S states, $1sns$ ${}^1S$ or $1sns$ ${}^3S$, of the He atom. Of these states, the Lamb shift of the lowest ionization potential of the $1s2s$ ${}^3S$ state was first calculated by Pekeris[10] to be -0.164 cm^{-1} and later by Suh and Zaidi[11] to be -0.109 cm^{-1}. The latter authors have determined the same quantity of the same atom in the $1s2s$ ${}^1S$ state to be -0.104 cm^{-1}. From our point of view derived in the preceding section, these values represent the contribution of the 2s electron to the Lamb shift of the respective states, since the 1s electron sees almost no screening from the 2s electron in these states and its contribution is just the same as the Lamb shift of the He^+ ion in its ground state. In order to see how much the screening effect is for the 2s electron we are dealing with, $\Delta E(2,0)$ as a function of Z has been established by fitting a cubic function of Z to the $\Delta E(2,0)$ value calculated with Eq. (2) for $Z = 1$, 2, 3, and 4. From the $\Delta E(2,0)$ vs Z function thus derived, it has been found that 0.164, 0.109, and 0.104 cm^{-1} quoted above correspond to the effective value of $Z = 1.51$, 1.3375, and 1.3200, corresponding to $s = 0.49$, 0.6625, and 0.6800, respectively. Of the three values of s, the first one is too small to be the screening effect of a 1s electron upon a 2s electron. The value 0.164 cm^{-1}, from which this value of s has been derived, was doubted by Pekeris himself[10] and has been replaced by 0.109 cm^{-1} of Suh and Zaidi.[11] The other two values of s seem to be reasonable.

We now go over to the excited states involving the np orbitals. There is no data available for such states comparable to those for the $1sns$ states. The radiative effect on the splitting among a triplet of a $1snp$ ${}^3P$ (n ${}^3P$) state may, how-

TABLE II. The radiative effect $\Delta(\Delta\nu_{01})$ on the fine structure splitting $\Delta\nu_{01}$ for the $1s2p\ ^3P$ and the $1s3p\ ^3P$ states of the He atom compared with the difference $\Delta[\Delta E(n,1)]$ between $\Delta E(n,1)$ calculated with Eq. (3) for two possible values of j (cm^{-1}).[a]

	$1s2p\ ^3P$	$1s3p\ ^3P$
$\Delta(\Delta\nu_{01})$[b]	1.824(− 3)	4.95(− 4)
$\Delta[\Delta E(n,1)]$		
$Z = 1.0$	0.8483(− 3)	2.514(− 4)
$Z = 1.2$	1.759(− 3)	5.212(− 4)

[a] Numbers in parentheses are the powers of ten by which the number should be multiplied.
[b] Reference 12.

ever, be used for checking the validity of our point of view in estimating the radiative effect upon the atomic energy levels involving a p orbital and the validity of Eq. (3) in estimating the contribution of a p electron to the radiative effect. In Table II, the radiative effect $\Delta(\Delta\nu_{01})$ on the splitting $\Delta\nu_{01}$ of the $2\ ^3P$ and the $3\ ^3P$ states of the He atom calculated by Pekeris *et al.*[12] are given. It is to be noted that the calculated value $\Delta\nu_{01}$ with radiative correction agrees with the experimental value[13,14] with an error of about $8\times10^{-5}\ cm^{-1}$ both for $2\ ^3P$ and $3\ ^3P$. From our point of view, the radiative effect upon each of the components of an $n\ ^3P$ state should be made up of the contributions from a $1s$ electron and an np electron and the effect upon $\Delta\nu_{01}$ may be regarded as the effect upon the different coupling schemes of an np electron with a $1s$ electron. The radiative effect upon $\Delta\nu_{01}$ of the $n\ ^3P$ state should therefore be comparable with the difference between the two values of $\Delta E(n,l)$ $(l = 1)$ from Eq. (3), one corresponding to $j = l + \frac{1}{2}$ and the other to $j = l - \frac{1}{2}$. Such a difference, denoted as $\Delta[\Delta E(n,1)]$, is also given in Table II for $Z = 1.2$ and $Z = 1$, corresponding to the screening effects of 0.8 and 1.0, respectively. It is to be noted that the $\Delta[\Delta E(n,1)]$ values with $Z = 1.2$ agrees fairly well with the respective $\Delta(\Delta\nu_{01})$ value although the former is smaller or larger than the latter, depending upon whether $n = 2$ or $n = 3$. This would imply that our scheme can estimate $\Delta(\Delta\nu_{01})$ if the screening effect of about $0.8(=2-1.2)$ is introduced and that the screening effect might be a little smaller than 0.8 for the $2p$ electron in the $2\ ^3P$ state while it might be a little larger than 0.8 for the $3p$ electron in the $3\ ^3P$ state. This magnitude of the screening effect is in consistent with the Slater rules.[7]

IV. CONCLUDING REMARKS

By analogy with or generalization of the results of the analysis for the two-electron atoms developed in the preceding two sections, it may be concluded that the radiative effect or the Lamb shift of a given state of a many electron atom is made up of one-electron quantities or contributions from individual electrons within the atom and that the one-electron contribution can be calculated at least approximately by the well known formula, quoted as Eqs. (2) and (3) in the present paper, for the radiative correction to energy levels of a hydrogen-like atom. It may also be concluded that "one-electron contribution" can be calculated adequately if the concept of an effective nuclear charge or the screening effect due to the other electrons within the atom is introduced. Actual numerical calculations using Eqs. (2) and (3) show that an s electron contributes much more to the radiative effect than a p electron, provided that the principal quantum numbers of the atomic orbitals containing these electrons are the same in consistent with the historic experiment by Lamb and Retherford.[15] As for s electrons, the contribution of a $1s$ electron is so important that the contributions of the other ns electrons $(n\geqslant2)$ are nearly negligible since $\Delta E(n,0)$ decreases in proportion to n^{-3} as Eq. (2) shows. Therefore, the radiative effect or the effect of the Lamb shift upon the ionization potential or the excitation energy may have to be considered only if a $1s$ electron is involved in the ionization or excitation. This conclusion is tacitly assumed in comparing the results of *ab initio* calculations of a reasonable accuracy on the atoms with $1s^22s^22p^m$ $(m = 0,1,...,6)$ configurations.[16] It may be claimed, however, that the conclusion has been obtained in the present work explicitly based upon a set of rather convincing evidence.

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