

Lamb Shift in Heliumlike Ions

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Estimates of the Lamb shift in bound states of two-electron ions reported by Kastner are discussed critically. A consistent treatment of the quantum-electrodynamical correction of order α^3 to the relativistic potentials of ionization of atoms with two electrons is developed and convenient expressions for these corrections in a $|nLSJ\rangle$ state of the atom are obtained. The numerical results are in close agreement with the experimental data of Edlén and Löfstrand for C V.

I. INTRODUCTION

Recently Kastner¹ has reported estimates of the lowest-order Lamb shift in some excited S , P , and D states of two-electron ions, based on the hydrogenic formulas for the shift.² His method suffers from a rather crude approximation to the part of the shift independent of the total angular momentum J of the atom and from an inaccurate treatment of the LSJ coupling which affects the part of the shift due to the anomalous magnetic moment of the electron.

As a consequence of these inaccuracies, the approach of Kastner is not generally capable of giving the correct result in the formal limit of high values of the nuclear charge Z . For low Z , any method based on the shift in hydrogen cannot lead to an accurate result even if the coupling is handled properly. This is due to an approximate treatment of the average excitation energy of the two-electron atom and due to the neglect of two-body terms appearing in the effective operator responsible for the shift of order α^3 of a two-electron atomic level. In this comment, we give a consistent treatment of the problem. The numerical results for the Lamb shift of the 2^1S_0 and 2^3S_1 levels, obtained by a simplified treatment of the shift, agree with the experimental values of Löfstrand³ for Be III, and Edlén and Löfstrand⁴ for C V within 30 and 10%, respectively. This indicates that for the ions with higher Z , the approximations adopted in the present work are certainly sufficient to match the accuracy of the experimental determination of the position of two-electron levels.

II. METHOD OF CALCULATION

For the total potential of ionization of a two-electron ion, I_t , we shall write

$$I_t = I_{\text{rel}} + E_I, \quad (1)$$

where I_{rel} is the potential to order α^2 (obtained in

the Breit-Pauli approximation) which also includes the energy corrections due to the finite mass of the nucleus, and E_I denotes the quantum-electrodynamical (QED) correction of order α^3 to the relativistic potential I_{rel} . For a $nLSJ$ state of a two-electron ion of nuclear charge Z ,

$$E_I = E_{L,1}(1s) - E_{L,2}(nLSJ), \quad (2)$$

where $E_{L,1}(1s)$ is the shift of order $Z^2\alpha^3\text{Ry}$ in the $|1s\rangle$ state of the hydrogenic ion of the same Z , and $E_{L,2}$ is the α^3 shift of the two-electron level.

We shall express $E_{L,1}$ as

$$E_{L,1}(nlj) = E'_{L,1}(nl) + E''_{L,1}(nlj), \quad (3)$$

where

$$E'_{L,1} = \frac{8\alpha^3 Z^4}{3\pi n^3} \left[\ln \frac{Z^2 \text{Ry}}{K_0(nl)} + \delta_{10} \left(2 \ln \frac{1}{\alpha Z} + \frac{19}{30} \right) \right] \text{Ry} \quad (4)$$

and

$$E''_{L,1} = \frac{\alpha^3 Z^4 (1 - \delta_{10}) C_{l,j}}{\pi n^3 (2l+1)} \text{Ry}, \quad (5)$$

$K_0(nl)$ being the modified average excitation energy,^{5,6} $C_{l,l+1/2} = (l+1)^{-1}$, and $C_{l,l-1/2} = -l^{-1}$.

We shall write $E_{L,2}$ in a way similar to that for $E_{L,1}$, namely,

$$E_{L,2} = E'_{L,2}(nLS) + E''_{L,2}(nLS) + E'''_{L,2}(nLSJ). \quad (6)$$

$E'_{L,2}$ is the proper Lamb shift and the vacuum-polarization correction in a two-electron ion.^{7,8} This term is of order $Z^2\alpha^3\text{Ry}$, and it is analogous to the hydrogenic shift [see Eq. (4)]. The term $E''_{L,2}$ comprises corrections of orders $Z\alpha^3$ and $Z\alpha^3 \ln \alpha \text{Ry}$ ^{8,9}:

$$E''_{L,2} = \alpha^3 \left[\delta^{(3)}(\vec{r}_{12}) \left(\frac{28}{3} \ln \alpha + \frac{178}{15} - \frac{40}{3} \vec{s}_1 \cdot \vec{s}_2 - \frac{28}{3} Q \right) \right] \text{Ry}, \quad (7)$$

where Q denotes the principal part of the logarithm

mically diverging quantity $\langle r_{12}^{-3} \rangle$, and $\langle A \rangle$ means the expectation value of A in the $|nLS\rangle$ state.

Finally, we define $E_{L,2}'''$ as the diagonal matrix element $\langle nLSJ | H_{L,2}'' | nLSJ \rangle$ of the operator $H_{L,2}''$,⁸ which we write as a sum thus:

$$H_{L,2}'' = (\alpha/\pi)(H_3''' + H_5'''), \quad (8)$$

where, in a.u.,

$$H_3''' = \frac{1}{4}\alpha^2 [Zr_1^{-3} \vec{r}_1 \times \vec{p}_1 + Zr_2^{-3} \vec{r}_2 \times \vec{p}_2 + 2Zr_{12}^{-3} \vec{r}_{12} \times (\vec{p}_1 - \vec{p}_2)] (\vec{s}_1 + \vec{s}_2) \quad (9)$$

and

$$H_5''' = \alpha^2 r_{12}^{-3} [\vec{s}_1 \cdot \vec{s}_2 - 3r_{12}^{-2} (\vec{r}_{12} \cdot \vec{s}_1)(\vec{r}_{12} \cdot \vec{s}_2)]. \quad (10)$$

$E_{L,2}''$ contributes to the fine-structure splitting. The notations in Eqs. (9) and (10) are the same as those in the fine-structure operators H_3 and H_5 of Bethe and Salpeter.² However, we note that H_3''' and H_5''' are not entirely identical to H_3 and H_5 .

Now we consider two useful approximations in the treatment of the difference $\delta E_L = E_{L,1} - E_{L,2}'$ and the term $E_{L,2}''$.

A. δE_L

In calculations of the term $E_{L,2}'$, the Bethe excitation energy $K_0(nLS)$ introduces the most difficult problem: an accurate value of $K_0(nLS)$ requires the knowledge of the oscillator strengths for transitions from the $|nLS\rangle$ state to all other stationary states of both the discrete spectrum and the continuum, which are not known in most cases.

For the ground state, we shall employ the hydrogenic approximation of Bethe and Salpeter²: $K_0 = 19.77Z^2$ Ry, which is usually considered as satisfactory for the ions with $Z \gtrsim 4$.^{7,15}

In the case of excited states, the usual way¹ to simplify the problem is to replace the Lamb shift in the two-electron ion by a sum of the shifts of the individual electrons. For the J -independent part of the total correction $E_{L,2}'$, this leads to $E_{L,2}' = E_{L,1}'(n_1 l_1) + E_{L,1}'(n_2 l_2)$, where $E_{L,1}'$ has been defined by Eq. (4). Consequently, for $n_1 = 1$, $l_1 = 0$, the difference $\delta E_L = E_{L,1}(1s) - E_{L,2}'$ appearing in Eq. (2) would become just $E_{L,1}'(n_2 l_2)$.

We note that the actual error brought in by this procedure comes from separate treatments of the atomic electrons in (i) the average excitation energy and (ii) the electron density near the nucleus, the latter being determined by $\langle \delta^{(3)}(\vec{r}_1) \rangle$. In order to reduce this error, we shall consider the high-frequency part $E_{L,2}'$ and the low-frequency part $E_{L,2}''$ of the term $E_{L,2}$ in two different approximations.

In $E_{L,2}'$, we use the expectation value of $\delta^{(3)}(\vec{r}_1)$

obtained with an accurate approximation to the $|nLS\rangle$ state. For $E_{L,2}''$, where the excitation energy K_0 appears, we resort to a hydrogenic approximation for both $\langle \delta^{(3)}(\vec{r}_1) \rangle$ and K_0 . Explicitly,

$$\begin{aligned} \delta E_L &= E_{L,1}(1s) - E_{L,2}'(1s, nl) \\ &= -\frac{8\alpha^3 Z}{3} \left[\frac{Z^3}{\pi} \Delta(Z) \left(2 \ln \frac{1}{\alpha Z} + \frac{19}{30} \right) - \frac{(Z-1)^3}{\pi n^3} \ln \frac{Z^2 \text{Ry}}{K_0(nl)} \right], \end{aligned} \quad (11)$$

where $\Delta(Z)$ denotes the relative departure of the electron density near the nucleus in a $|nLS\rangle$ state of a two-electron ion from that in a $|1s\rangle$ state of the hydrogenic ion of the same Z :

$$\Delta(Z) = \frac{2\pi \langle \delta^{(3)}(\vec{r}_1) \rangle}{Z^3} - 1. \quad (12)$$

For low Z , the term $E_{L,2}'$, which is determined in Eq. (11) more accurately than $E_{L,2}''$, gives the main contribution to the shift $E_{L,2}'$. For higher Z , the relative importance of the low-frequency part $E_{L,2}''$ increases. However, the hydrogenic approximation itself is more adequate in the latter case. In the high- Z limit, Eq. (11) reduced to the "simple hydrogenic approximation" employed particularly in Ref. 1.

B. $E_{L,2}''$

According to formulas (9) and (10), the anomalous magnetic moment term $E_{L,2}''$ can be expressed in terms of integrals usually employed in the fine-structure calculations. For high values of the nuclear charge Z , the coupling between the spin and the orbital momentum of the same electron due to the Coulomb field of the nucleus dominates over other J -dependent effects. As a result, the transformation properties of $H_{L,2}''$ and the fine-structure operator become identical, so that a simple replacement of \vec{s}_i by $(1 + \alpha/\pi)\vec{s}_i$ in the latter would account for the leading term in $E_{L,2}''$, which is of order $Z^2\alpha^3$ (note that this has not been done in Ref. 1). For low Z , $H_{L,2}''$ is no longer proportional to the fine-structure operator, an effect which does not arise, in the corresponding α^3 order, in one-electron atoms at all. In the case of ions with very low Z ($Z \lesssim 4$), the calculation of $\langle H_{L,2}'' \rangle$ requires quite accurate nonrelativistic wave functions of the Hylleraas type.^{10,11} However, for higher Z a less sophisticated treatment which employs hydrogenic wave functions is practically sufficient. Furthermore, for $L \neq 0$ (otherwise $E_{L,2}''$ vanishes identically), one can neglect the exchange integrals and replace $|1s\rangle$ by $\delta(\vec{r}_1)$ all together: this procedure for $E_{L,2}''$ is justified by similar fine-structure calculations.^{2,12} In this

way, we obtain

$$\langle nL1J|H_{L,2}''|nL1J\rangle = \frac{(A_{LJ}Z + B_{LJ})(Z-1)^3\alpha^3}{\pi n^3 L(L+1)(2L+1)} \text{Ry} \quad (13)$$

and

$$\langle nL0J|H_{L,2}''|nL0J\rangle = 0, \quad (14)$$

where

$$\begin{aligned} A_{LJ} &= L, & J=L+1 \\ &= -1, & J=L \\ &= -(L+1), & J=L-1 \end{aligned} \quad (15)$$

and

$$\begin{aligned} B_{LJ} &= -4L(L+1)/(2L+3), & J=L+1 \\ &= 0, & J=L \\ &= 4L(L+1)/(2L-1), & J=L-1. \end{aligned} \quad (16)$$

The effect of coupling between different $nLSJ$ states due to the spin-orbit and spin-spin interactions has already been discussed by Ermolaev and Jones.¹³ It has been shown that the coupling between the singlet and triplet P states appreciably influences the fine-structure intervals ν_{21} and ν_{01} even for low Z , $Z \approx 6$. In the present scheme for P states, which introduces terms of order α^3 into the total Hamiltonian as well, both effects (the singlet-triplet interaction and the QED correction) should be treated simultaneously. For this, the total energy matrix has to be diagonalized.¹⁴ The singlet-triplet correction to I_{rel} , which incorporates the effects of diagonalization, is then given by $\epsilon_{\text{st}} = (-1)^{S+1} E_{\text{st}}$, where the quantity E_{st} is defined according to

$$E_{\text{st}} = \langle n111|H_t|n111\rangle - \lambda_{\text{min}} > 0, \quad (17)$$

λ_{min} being the smaller root of the secular equation.

III. RESULTS AND DISCUSSION

The correction E_I has been calculated for 1^1S_0 , 2^1S_0 , 2^3S_1 , and $2^{1,3}P_1$ states of two-electron ions where very accurate values of the relativistic potentials I_{rel} are known in a wide range of Z .¹⁵⁻¹⁸

The present calculations require accurate expectation values of the δ functions and estimates of the Q term in Eq. (7). The expectation values of $\delta^{(3)}(\vec{r}_1)$ and $\delta^{(3)}(\vec{r}_{12})$ for $Z \geq 11$ have been obtained by an interpolation procedure described earlier,¹⁹ from the data^{15,16} for $Z \leq 10$.

For the ground state, accurate values of Q have been obtained in two successive sets of calculations. First, we computed Q for $Z=2, 3, 8$, and 12 employing 20-parameter Hylleraas functions.²⁰ These values of Q were used then to obtain $Q(Z)$

for other members of the sequence by the interpolation method.¹⁹ Particularly, $Q(2) = -0.0715 \text{ cm}^{-1}$ and $Q(3) = -0.463 \text{ cm}^{-1}$. For He I, the result corresponds with -0.072 of Sucher⁹ and with -0.0685 cm^{-1} of Dalgarno and Stewart,²¹ who used less accurate wave functions. For $Z \geq 3$, this small correction has not been estimated before, either for the ground state or for the excited states of two-electron ions.

We note that the Q term can be written as

$$Q = \ln(Z_i + Z_a/n) \langle \delta^{(3)}(\vec{r}_{12}) \rangle + Q', \quad (18)$$

where Z_i and Z_a are effective nuclear charges for the inner and outer electrons, respectively, and the term Q' is of order Z^3 . In the present calculations of Q for the excited states of two-electron ions, the nuclear charges were set $Z_i = Z$ and $Z_a = Z - 1$. $Q'(Z)$ is relatively small even for the ground state: $Q'(4) = -0.14$ and $Q'(6) = -0.53 \text{ cm}^{-1}$ to be compared with $Q(4) = -1.52$ and $Q(6) = -7.23 \text{ cm}^{-1}$. Consequently, the term Q' was neglected in the reported estimates of Q for the excited states.

In addition to the calculations of E_I (and ϵ_{st}) reported in this work, we have also computed the volume-isotope shift ΔV_I of the ionization potentials of two-electron ions:

$$\Delta V_I = -\frac{4}{3} Z^4 \Delta(Z) \delta_{\text{nucl}} \text{Ry}, \quad (19)$$

where $\delta_{\text{nucl}} = \langle r_{\text{nucl}}^2 \rangle / a_0^2$, r_{nucl} and a_0 being the nuclear

TABLE I. The ground state of two-electron ions: the QED corrections, and the volume-isotope correction ΔV_I to the relativistic potentials I_{rel} . All quantities are given in cm^{-1} .

Z	Isotope	E_I^a	\tilde{Q}^b	ΔV_I
4	Be ⁹	-27.1	-1.52	-0.04
5	B ¹¹	-65.7	-3.64	-0.12
6	C ¹²	-132.2	-7.23	-0.28
7	N ¹⁴	-235	-12.8	-0.70
8	O ¹⁶	-385	-20.6	-1.14
9	F ¹⁹	-584	-31.4	-2.10
10	Ne ²⁰	-844	-45.5	-3.36
12	Mg ²⁴	-1571	-85.7	-8.01
14	Si ²⁸	-2602	-145	-16.8
20	Ca ⁴⁰	-7540	-485	-91.5
26	Fe ⁵⁶	-14 010	-1160	-128
30	Zn ⁶⁴	-17 290	-1860	-728

^a The Kabir and Salpeter terms (Ref. 7); the Q term is not included. For $Z \leq 10$, Pekeris (Ref. 15); for $Z > 10$, present calculations.

^b $\tilde{Q} = \frac{2}{3} \alpha^3 Q \text{ Ry}$.

TABLE II. $2^{1,3}S$ states of two-electron ions: the QED corrections and the volume-isotope correction ΔV_I to the relativistic potentials of ionization I_{rel} . All quantities are given in cm^{-1} .

Z	2^1S_0			2^3S_1		
	δE_L	$-E''_{L,2}$	E_I	ΔV_I	$E_I(=\delta E_L)$	ΔV_I
4	-3.36	0.07	-3.28	-0.004	-4.07	-0.004
5	-8.44	0.12	-8.31	-0.012	-9.93	-0.014
6	-17.4	0.17	-17.2	-0.030	-20.0	-0.033
7	-31.5	0.19	-31.3	-0.065	-35.7	-0.070
8	-52.0	0.15	-51.8	-0.13	-58.3	-0.14
9	-80.1	0.02	-80.1	-0.23	-89.1	-0.25
10	-117	-0.2	-117	-0.38	-129	-0.40
12	-222	-1.2	-223	-0.93	-242	-0.97
14	-373	-3.0	-377	-1.96	-405	-2.04
20	-1145	-17	-1160	-10.9	-1230	-11.2
26	-2320	-52	-2370	-40.0	-2490	-40.9
30	-3150	-93	-3240	-78.5	-3400	-80.1

radius²² and the Bohr radius, respectively; $\Delta(Z)$ has been defined by formula (12).

The numerical results for E_I , ϵ_{st} , and ΔV_I are presented in Tables I, II, and III.

The new values of E_I for the ground state (Table I) differ by 5–8% from those previously reported by Pekeris,¹⁵ who omitted the Q term for $Z > 2$.

In the case of excited S states (Table II), E_I is generally given by $\delta E_L - E''_{L,2}$ as $E''_{L,2}$ vanishes for $L=0$. According to Eq. (9), the difference between the numerical values of δE_L , for the singlet and triplet S states of an ion, is entirely due to $\Delta(Z)$. With Z increasing, δE_L approaches the same high- Z limit in both 2^1S_0 and 2^3S_1 states. This follows from the asymptotic behavior of $\Delta(Z)$: $\Delta(Z) = n^{-3} + O(Z^{-1})$. The term $E''_{L,2}$, which includes a correction to the electron-electron interaction, is proportional to $\langle \delta^{(3)}(\vec{r}_{12}) \rangle$ and therefore it does

not contribute to the shift in triplet S states.

In the case of P states (Table III), the situation is more intricate. The δE_L term, for any $L \neq 0$ state, is mainly determined by the departure of $|nLS\rangle$ from the superposition of two hydrogenic states, that is, by $\Delta(Z)$. This is due to the smallness of the one-electron Lamb shift $E'_{L,1}(nl)$ for $l \neq 0$: the high-frequency part of the shift $E'_>=0$ as the electron density at the nucleus is zero in a $l \neq 0$ state; the low-frequency part $E'_<$ of the shift is small, as the average excitation energy $K_0(nl)$ is small for $l \neq 0$.⁶ For $L \neq 0$ states, the function $\Delta(Z)$ is of order Z^{-1} as Z increases. However, for low Z , $\Delta(Z)$ appreciably departs from zero, being positive for singlet P states and negative for triplet P states, and it leads to δE_L , presented in Table III. As in the case of S states, the term $E''_{L,2}$ contributes only to the shift of the singlet P

TABLE III. $2^{1,3}P_1$ states of two-electron ions: the singlet-triplet correction E_{st} , the QED corrections, and the total correction $\epsilon_I = E_I + (-1)^{S+1}E_{st}$ to the relativistic potentials of ionization I_{rel} .^a All quantities are given in cm^{-1} .

Z	2^1P_1				2^3P_1		
	E_{st}	δE_L	$-E''_{L,2}$	ϵ_I	δE_L	$-E''_{L,2}$	ϵ_I
4	0.043	-0.191	0.014	-0.220	0.954	0.031	1.03
5	0.224	-0.442	0.028	-0.638	1.95	0.090	2.27
6	0.850	-0.840	0.041	-1.65	3.41	0.21	4.47
7	2.60	-1.42	0.046	-3.97	5.36	0.43	8.39
8	6.82	-2.21	0.038	-8.99	7.87	0.78	15.5
9	15.9	-3.25	0.005	-19.1	11.0	1.30	28.1
10	33.7	-4.59	-0.060	-38.3	14.6	2.06	50.4
12	123	-8.28	-0.34	-131	23.9	4.5	151
14	363	-13.6	-0.88	-377	35.6	8.7	406
20	4160	-43.8	-5.2	-4210	85.0	39	4280
26	22 100	-105	-16	-22 220	149	115	22 360
30	50 970	-172	-29	-51 170	194	207	51 370

^a The volume-isotope shift of $2^{1,3}P$ potentials of ionization has been omitted. For $4 \leq Z \leq 30$, ΔV_I ranges from -0.00014 to -0.46 cm^{-1} in the case of singlet P states, and from 0.00079 to 1.85 cm^{-1} in the case of triplet P states.

TABLE IV. The term system in C v. Comparison between the experimental and theoretical potentials of ionization. All quantities are given in cm^{-1} .

Term	Previous results		Present results	
	I_{theor}	I_{expt}	I_{theor}^a	I_{expt}
1^1S_0	3 162 441 ^b	3 162 385 ± 37 ^c 3 162 398 ± 36 ^d	3 162 433	3 162 383 ± 37 ^c 3 162 403 ± 36 ^d
2^1P_1	679 024 ^e	679 024 ^f	679 022	679 022 ^f
2^1S_0	707 387 ^e	707 371 ± 4 ^g	707 370	707 369 ± 4 ^g
2^3S_1	751 149 ^e	751 133 ± 4 ^h	751 129	751 128 ± 4 ^h
2^3P_1	707 241 ^e	707 247 ± 5 ⁱ	707 246	707 242 ± 5 ⁱ

^a $I_{\text{theor}}=I_t$ of present work, which includes terms of order α^3 and ϵ_{st} .

^b $I_{\text{theor}}=I_{\text{rel}}+E_I$ of Ref. 15 (E_I does not include the Q term).

^c From $T_{\text{expt}}(2^1P_1-1^1S_0)$ of Ref. 4 and theoretical 2^1P_1 .

^d From $T_{\text{expt}}(2^3P_1-1^1S_0)$ of Ref. 4 and theoretical 2^3P_1 .

^e $I_{\text{theor}}=I_{\text{rel}}$ of Ref. 23 (terms of order α^3 and ϵ_{st} are not included).

^f Theoretical 2^1P_1 has been adopted.

^g From $T_{\text{expt}}(2^1P_1-2^1S_0)$ of Ref. 4.

^h From $I_{\text{expt}}(2^1S_0)$ and theoretical $T(2^1S_0-2^3S_1)$.

ⁱ From $I_{\text{expt}}(2^3S_1)$ and $T_{\text{expt}}(2^3P_1-2^3S_1)$ of Ref. 4.

level. On the contrary, the anomalous magnetic-moment term $E_{L,2}''$ gives a contribution only to the triplet P level which follows from Eqs. (11) and (12). Finally, the interaction between the singlet and triplet P states results in an additional correction ϵ_{st} , formula (15). In the case of ions with low Z ($Z \leq 10$), all these corrections are of the same order of magnitude, and, therefore they should be applied to I_{rel} all together. For higher Z , the singlet-triplet interaction ϵ_{st} dominates over the QED correction E_I .

We note that in the calculations of Accad *et al.*,^{16,23} the relative position of the $J=0$ and $J=2$ triplet P levels, with respect to the $J=1$ component, was determined to order α^3 . However, the absolute position of the $J=1$ level itself was given less accurately,²⁴ to order α^2 only, with ϵ_{st} being omitted as well. Consequently, the ν_{21} and ν_{01} intervals reported in Ref. 16 need be corrected with respect to ϵ_{st} only,²⁵ whereas the 3P_1 potentials I_{rel} must be corrected with respect to both ϵ_{st} and E_I .

It is instructive to reexamine the term system

TABLE V. The Lamb shift of 2^1S terms in Be III and C v: comparison between theory and experiment. All quantities are given in cm^{-1} .

Term	Be III		C v	
	Theory	Expt. ^a	Theory	Expt. ^b
2^1S_0	-3.2	-3.1 ± 0.1	-17.2	-18 ± 4
2^3S_1	-4.1	-3.2 ± 0.2	-20.0	-17 ± 1

^a Reference 3.

^b Reference 4.

in C v studied by Edlén and Löfstrand.⁴ In the derivation of the experimental position of levels in C v, these authors adopted theoretical values of the $2^1P_1-2^3P_1$ potentials of ionization and the $2^3S_1-2^1S_0$ separation which had been obtained (to order α^2) by Accad *et al.*²³ The results of the Edlén and Löfstrand analysis are presented in the first two columns of Table IV. We have corrected the theoretical potentials with respect to E_I and ϵ_{st} (the volume-isotope shift does not practically affect the position of the levels). Our results are presented in the last two columns of Table IV. For the ground state, the agreement is improved mainly due to the Q correction. The remaining discrepancy between theory and experiment can probably be attributed to higher-order corrections ignored in the present calculations, and, partly, to the inaccuracy of the hydrogenic value of K_0 .²⁶ For $n=2$, the agreement between theory and experiment is within the experimental errors.

For low Z the approximations adopted in the present work are expected to introduce larger errors. The analysis of the term system in C v shows that the present method is likely to be quite adequate to treat the Lamb shift in the ions with $Z \geq 6$. Now we shall consider the case of Be III ($Z=4$), where new very accurate experimental data are available due to Löfstrand.³

In view of a relatively small magnitude of the Lamb shift in $L=1$ states, we can neglect, in the P potentials, the errors in E_I owing to the approximations introduced in this work. This can be used to estimate the accuracy of our numerical values of the shift $1s2s$ S states. We define the experimental Lamb shift $E_{I,\text{expt}}$ of the 2^1S_0 potential of ionization according to

TABLE VI. 1^1S , 2^1S and 2^1P_1 states of two-electron ions: the total potentials of ionization I_t (cm^{-1}).^a

Z	Isotope	1^1S_0	2^1S_0	2^3S_1	2^1P_1	2^3P_1
11	Na ²³	11 816 996	2 789 014	2 881 659	2 728 296	2 794 129
12	Mg ²⁴	14 210 175	3 371 140	3 473 757	3 303 283	3 377 083
13	Al ²⁷	16 824 908	4 008 780	4 121 446	3 933 431	4 015 424
14	Si ²⁸	19 661 546	4 702 047	4 824 843	4 618 760	4 709 255
20	Ca ⁴⁰	41 369 118	10 038 335	10 223 959	9 892 082	10 045 460
22	Ti ⁴⁸	50 404 639	12 269 626	12 477 122	12 093 086	12 275 467
26	Fe ⁵⁶	71 208 463	17 421 218	17 674 159	17 161 103	17 423 455
27	Co ⁵⁹	76 983 563	18 854 128	19 118 823	18 567 016	18 855 383
28	Ni ⁵⁸	82 990 052	20 345 575	20 622 193	20 028 533	20 345 870
29	Cu ⁶³	89 229 020	21 895 884	22 184 601	21 545 739	21 895 238
30	Zn ⁶⁴	95 701 337	23 505 325	23 806 324	23 118 628	23 503 795
42	Mo ⁹⁸	191 990 240	47 558 140	48 023 130	46 359 520	47 551 840

^a The volume-isotope shift ΔV_I has not been included.

$$E_{I, \text{expt}}(2^1S_0) = I_t(2^1P_1) + T_{\text{expt}}(2^1P_1 - 2^1S_0) - I_{\text{rel}}(2^1S_0), \quad (20)$$

with an analogous expression holding for $E_{I, \text{expt}}(2^3S_1)$. T_{expt} denotes the experimental separation between corresponding S and P levels. The difference $E_{I, \text{expt}} - E_I$ can then be interpreted as a probable error in E_I .

In Table V, we present a comparison between the theoretical and experimental values of the Lamb shift in 2^1S states of Be III and C V. It can be seen that in the case of Be III the probable error in E_I constitutes 30%, which exceeds the experimental error by a factor of three. For C V, theory and experiment agree with each other within 10%, which corresponds with the experimental error in this case. We attribute the discrepancy observed in the case of Be III to a breakdown of the present method, avoiding a direct calculation of $K_0(nLS)$, for low Z .

In view of possible applications of the data reported in this work, in plasma and solar flare spectroscopy, we present in Table VI the total ionization potentials I_t for some highly ionized two-electron atoms with $Z > 10$. These ions have been observed in recent experiments.²⁷ In the calculations of I_t , the relativistic term I_{rel} has been obtained in Ref. 18 by the method of Ref. 19. The estimated accuracy of I_{rel} is of order 1 ppm. The probable error in our values of E_I and ϵ_{st} is of order 10%. This leads to an error of order 10 ppm for I_t , which is appreciably smaller than that of the present experimental determination of the position of the levels in two-electron ions with $Z > 10$.

We note that Table VI shows an apparent irregularity in the position of the 2^3P_1 level with respect

to the 2^1S_0 level, as Z increases. This effect is due to a different Z dependence of the relativistic and the singlet-triplet interactions both competing with correlation effects in the ion of high Z .

Contributions of orders higher than α^3 as well as those of order $(m/M)\alpha^3$ have not been considered in this work. For the ground state of the ions with low Z , these corrections will probably be of some experimental significance. When accurate experimental data for the ions of high Z are available, it will also allow one to form a more definite opinion on the actual range of Z , within which the theory based on the perturbation treatment of the Breit-Pauli and Lamb-shift terms is a good approximation.

Finally, we note that the effective Lamb-shift operator which includes one- and two-body terms can be introduced into the Hamiltonian of an N -electron atom in the same way as it has been done in the two-electron case. It will be of interest to have accurate values of K_0 in a wider range of ions and states so that the present approximation for δE_L could be tested so as to apply it to an N -electron atom. As to the operators $H_{L,2}'''(\vec{r}_i, \vec{r}_k)$: their inclusion would only require a slight modification of the part of the existing atomic-structure programs²⁸ which is concerned with the fine-structure splitting.

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- ²⁴This would correspond with direct measurements of the fine-structure intervals ν_{21} and ν_{01} . However, the present experimental values of the intervals in two-electron ions are derived from the $2^3S_1-2^3P_J$ transitions and, therefore, it is more consistent to apply the corrections to all levels in question.
- ²⁵Corrected intervals ν_{21} and ν_{01} in 2^3P and 3^3P states of some two-electron ions are given in Ref. 13.
- ²⁶In Ref. 4, Edlén and Löfstrand observed a discrepancy of $45 \pm 30 \text{ cm}^{-1}$ between the theoretical and experimental position of the 1^1S_0 level in C v. They suggested that the Lamb shift of -132 cm^{-1} reported by Pekeris in Ref. 15 was too small. The Q correction included in E_I in the present calculation contributes to the Lamb shift an additional amount of -7.2 cm^{-1} which accounts only for 50% of the discrepancy. The new experimental data of Löfstrand (Ref. 3) reveal that the similar situation occurs in the ground term of Be III. The Q correction which contributes -1.5 cm^{-1} to the shift cannot be the only source of the discrepancy of $19 \pm 15 \text{ cm}^{-1}$ found in the ground term of Be III. The main source of uncertainty in the present theoretical values of the 1^1S Lamb shift is the hydrogenic approximation employed in calculations of K_0 . If we extrapolate accurate values of K_0 for $Z = 2, 3$ (Ref. 7) to $Z = 4$ and 6, we shall find that this approximation can lead to an error of a few percent in the value of the Lamb shift. This amount is comparable to the magnitude of higher-order QED corrections. In the cases of Be III and C v, more accurate calculations of K_0 as well as estimates of the higher-order QED corrections are desirable in order to establish the source of the present discrepancy between theory and experiment.
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Erratum

Self-Diffusion in Krypton at Intermediate Density, P. Carelli, I. Modena, and F. P. Ricci [Phys. Rev. A **7**, 298 (1973)]. The D and $D(220/T)^{0.9}$ of the head line of Table I must be multiplied by 10^{-4} .