Asymptotic Lamb Shifts for Helium Rydberg States

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(Received 8 January 1992)

A global formula for the asymptotic Lamb shifts of the Rydberg states of helium is obtained by calculating the electric field perturbation due to the Rydberg electron on the $\mathrm{He}^+(1s)$ Lamb shift. The result substantially reduces theoretical uncertainties in calculated transition frequencies. A comparison with experiment for transitions among the $n=10$ states of helium reveals systematic discrepancies much larger than expected corrections due to higher-order relativistic and Casimir-Polder effects.

PACS numbers: 31.20.Di, 31.30.Jv, 31.50.+w

The accuracy of both theory [1,2] and experiment [3] for transition frequencies among the Rydberg states of helium has now advanced to the point that the comparison is sensitive to both the Lamb shift (i.e., electron self-energy and vacuum polarization) and long-range Casimir-Polder retardation corrections [4–6]. Both are quantum electrodynamic (QED) effects, with the latter being (in lowest order) a correction to short-range approximations to the retarded Breit electron-electron interaction energy. For a Rydberg electron with radial coordinate x in the range $a_0 \ll x < a_0/\alpha$, the leading retardation term is proportional to $e^2\alpha^2 a_0^3/x^4$; but for $x \gg a_0/\alpha$, the predicted power-law dependence changes to $e^2\alpha a_0^4/x^5$ (a_0 is the Bohr radius and α the fine-structure constant). The helium Rydberg states provide a precise test of QED in a system containing more than just a single electron in the Coulomb field of the nucleus. The comparison between theory and experiment provides an opportunity to verify the smaller Casimir-Polder effects if the Lamb shift corrections are sufficiently well understood.

Many years ago, Kabir and Salpeter [7] obtained the lowest-order Lamb shift for helium. In atomic units, it differs from the one-electron case only in the replacement of the usual Bethe logarithm by the corresponding two-electron quantity (see below), and the overall multiplying factor of $\langle \nabla^2 V \rangle$, where $V=-Z/r$ is the nuclear Coulomb potential, becomes the two-electron expectation value $\langle \delta(\mathbf{r}_1)+\delta(\mathbf{r}_2) \rangle$ instead of $Z^3/\pi n^3$. The final result, relative to the one-electron ion, is

$$\Delta E_{L,1} = \tfrac{4}{3} Z\alpha^3 \langle \delta(\mathbf{r}_1)+\delta(\mathbf{r}_2) \rangle \{ \ln(Z\alpha)^{-2} + \ln[Z^2 R_M/k(nLS,Z)] + \tfrac{19}{30} + 2.296\pi\alpha Z + (\mu/M)C_M \} - \Delta E_L(1s) \tag{1}$$

for an LS-coupled state with principal quantum number n. $\Delta E_L(1s)$ is the corresponding one-electron Lamb shift which is common to all states, and $(\mu/M)C_M$ contains finite-mass terms. This and the $\pi\alpha Z$ term are small ($\sim 2\%$) corrections well known from the one-electron Lamb shift. The two-electron Bethe logarithm (BL) for nuclear charge Z is defined by

$$\ln[Z^2 R_M/k(nLS,Z)] = A/D \tag{2}$$

with

$$A = \sum_k |\langle \Psi_0 | \mathbf{p}_1 + \mathbf{p}_2 | \Psi_k \rangle|^2 (E_k - E_0) \ln 2(E_k - E_0)\,, \tag{3}$$

$$D = \sum_k |\langle \Psi_0 | \mathbf{p}_1 + \mathbf{p}_2 | \Psi_k \rangle|^2 (E_k - E_0)\,. \tag{4}$$

The denominator of (2) can be simply evaluated by use of the sum rule

$$D = 2\pi Z \langle \delta(\mathbf{r}_1) + \delta(\mathbf{r}_2) \rangle\,, \tag{5}$$

but there is no corresponding simple sum rule for A. A direct summation over intermediate states is difficult because there are large contributions from highly excited states and the two-electron continuum. A recent dramatic advance in accuracy has been achieved for the low-lying ^1S states by the use of sophisticated finite basis set methods [8], but for the higher-L states, the best estimates are based on a simple screened hydrogenic approximation [2,9]. The purpose of this Letter is to apply the methods of asymptotic analysis to obtain a global result for the two-electron BL that becomes essentially exact in the limit of high-L states. The results substantially reduce theoretical uncertainties for transitions among the $n=10$ states of helium.

The starting point for the calculation is the physical picture of a helium atom with a Rydberg electron in a high-nL state moving in the field of a polarizable core with effective charge $Z-1$ consisting of the nucleus with charge Z and a tightly bound inner $1s$ electron. For a sufficiently highly excited state, exchange effects can be neglected and the electrons treated as distinguishable. Denoting the position vectors of the inner and outer electron by $\mathbf{r}$ and $\mathbf{x}$, respectively, the corresponding nonrelativistic Hamiltonian is

$$H = \left[-\frac{1}{2}\nabla_r^2 - \frac{Z}{r} \right] + \left[-\frac{1}{2}\nabla_x^2 - \frac{Z-1}{x} \right] + V(\mathbf{r},\mathbf{x})$$

$$\equiv h_r + h_x + V(\mathbf{r},\mathbf{x}) \tag{6}$$

with

$$V(\mathbf{r},\mathbf{x})=1/|\mathbf{x}-\mathbf{r}|-1/x\,. \tag{7}$$

The eigenvalues of h_r+h_x are $-Z^2/2-(Z-1)^2/2n^2$; and treating $V(\mathbf{r},\mathbf{x})$ as a perturbation gives the leading polarization correction $-\frac{1}{2}\alpha_1\langle x^{-4}\rangle_{nL}$, where α_1 is the core polarizability.

In the same one-electron screening approximation, the asymptotic expansion for D is known to be [10], from the sum rule (5),

$$D=2Z^4-\frac{31}{Z^2}\langle x^{-4}\rangle_{nL}+\frac{1447}{8Z^4}\langle x^{-6}\rangle_{nL}+O(\langle x^{-7}\rangle_{nL})\,. \tag{8}$$

The leading term of A can also be simply evaluated by writing the wave functions in (3) as products of screened hydrogenic wave functions and taking advantage of the one-electron properties of the transition operator, with the result [9]

$$A=2Z^4\{\beta_{1s}+[(Z-1)^4/Z^4n^3]\beta_{nL}\}+\Delta A_{\rm pol}\,, \tag{9}$$

where $\beta_{nL}=\ln[k_0(nL)/R_M]$ is the hydrogen atom BL [9], and $\Delta A_{\rm pol}$ is the polarization correction to β_{1s} due to the electric field of the Rydberg electron. Since the energy shift of He$^+(1s)$ in an external dipole field of strength F is by definition $-\frac{1}{2}\alpha_1F^2$, the effective field strength (in a.u.) at the nucleus due to the Rydberg electron is $F^2=\langle x^{-4}\rangle_{nL}$. Treating Fz as a perturbation of $\psi_0(1s)$ up to second order gives

$$\psi_2(1s)=F^2(-\tfrac{31}{2}+\tfrac{3}{2}r^2+\tfrac{1}{2}r^3+\tfrac{1}{12}r^4)Y_0^0(\hat{\mathbf{r}})e^{-r}$$
$$+D\text{ wave}\,,$$

normalized to unity up to order F^2. The matrix element $4\pi Z\langle\psi_0|\delta(\mathbf{r})|\psi_2\rangle$ then yields directly the second term in Eq. (8). It follows that $\Delta A_{\rm pol}$ also has the form $A_4\langle x^{-4}\rangle_{nL}$, where A_4 is an unknown perturbation coefficient. We have not been able to find a convergent scheme for calculating A_4 by perturbation theory because the highly excited states in Eq. (3) are strongly perturbed, even for weak fields. The use of parabolic coordinates helps to simplify the calculation, but the bound-state sum over n still diverges as n^3.

To summarize, the problem is to calculate the change in β_{1s} due to the presence of an external electric field. To circumvent the divergent perturbation sums, we replace the actual intermediate states by finite basis sets in parabolic coordinates $\xi=r+z$ and $\eta=r-z$. The basis sets are a generalization of those used previously in BL calculations [11]. The explicit form is

$$\varphi_{ijk}=(\xi-\eta)^i(\xi+\eta)^j(\xi\eta)^{|m|/2}\exp[-\lambda_k(\xi+\eta)]\,. \tag{10}$$

For the ground state, $2\lambda_k=1$, and i and j both run from 0 to 6 for a total of 49 basis functions. For the excited states there are two sectors. The first is the same as the above, except that $i=-1,0,\dots,5$ for $m\neq0$ (m is the magnetic quantum number). In the second sector, $j=0,1,2$; $i=0,1,2$ ($i=-1,0,1$ for $m\neq0$), and $2\lambda_k$ follows the exponential distribution

$$2\lambda_k=\exp(2.75x_{k-1})^{0.6},\quad k=2,\dots,18\,, \tag{11}$$

where the x_k are the zeros of a Laguerre polynomial of order 18. These functions are necessary in order to cover a wide range of distance scales and obtain convergent results with basis set size. The total Hamiltonian, including the Fz term, is then diagonalized and the resulting pseudospectrum used to perform the summations over intermediate states. The final step is to determine A_4 by extracting the coefficient of F^2 from the BL calculated for a range of finite field strengths. A firm control over the accuracy of the calculation is provided by simultaneously calculating the coefficients in the corresponding D_4 expansion,

$$D_4=D_4^{(2)}F^2+D_4^{(4)}F^4+\cdots\,, \tag{12}$$

where, from (8), $D_4^{(2)}=-31$ (for $Z=1$), and the exact values for the higher-order terms are

$$D_4^{(4)}=-12\,303/8,\quad D_4^{(6)}=-13\,109\,865/64\,,$$
$$D_4^{(8)}=-90\,205\,710\,189/2048\,.$$

Table I compares these with the values obtained from a least-squares fit to the finite basis set calculations, with F^2 in the range $10^{-8}\leq F^2\leq10^{-4}$. The good agreement even for the higher-order terms gives confidence that the spectrum of intermediate states is adequately represented. As a further check, all calculations were done in both the "velocity" and "acceleration" ($\mathbf{p}\to i\nabla V/\Delta E$) gauges. The two agree, although the latter is more rapidly convergent. The convergence of the "length" form is poor.

The only change needed to calculate $\beta_{1s}(F)$ is to add an extra factor of $\ln\Delta E$ in the sum over states. The result is

$$\beta_{1s}(F)=2.984\,128\,556+0.316\,262(1)F^2$$
$$+24.61(1)F^4+O(F^6)\,, \tag{13}$$

with F^2 replaced by $\langle x^{-4}\rangle_{nL}$ for the Rydberg states of helium. Expanding the denominator into the numerator of (2), and using (8) and (9), the final result for the two-

TABLE I. Comparison of exact expansion coefficients $D_4^{(j)}$ [see Eq. (12)] with the finite basis set results (in a.u.).

Coefficient	Exact	Finite basis set
$D_4^{(2)}$	−31.000000	−31.0000000003(3)
$D_4^{(4)}$	−1537.875000	−1537.87494(3)
$D_4^{(6)}$	−204841.640625	−204815.6(1.0)
$D_4^{(8)}$	-4.404575693×10^7	$-4.391(2)\times10^7$
$D_4^{(10)}$	$-1.339570593\times10^{10}$	$-1.48(1)\times10^{10}$

electron BL is

$$\ln[k_0(1snL,Z)/Z^2R_M]=\beta_{1s}+\frac{(Z-1)^4}{Z^4n^3}\beta_{nL}+Z^{-6}\left[0.31626+\frac{31}{2}\left(\frac{Z-1}{Z}\right)^4 n^{-3}\beta_{nL}\right]\langle x^{-4}\rangle_{nL}\,. \tag{14}$$

The second term in square brackets is negligible, as are corrections to β_{nL} due to the action of the $-\frac{1}{2}\alpha_1/x^4$ polarization potential on the Rydberg electron.

Equation (14) is a global result that applies to all Rydberg states with $L>0$. It rapidly improves in accuracy with increasing L, and becomes exact in the high-L limit. Of particularly important significance is the fact that it removes the largest source of uncertainty in previously published [1,2] high precision variational calculations for the Rydberg states of helium up to $n=10$ and $L=7$. The extra contribution that should be added to these results due to the polarization of β_{1s} is

$$\Delta E_{L,\beta}=-\frac{4\alpha^3}{3\pi Z^2}0.31626\langle x^{-4}\rangle_{nL}\,. \tag{15}$$

Table II gives values of $\Delta E_{L,\beta}$ for a representative sample of states. For $L=1$, the value tabulated is $0.5\Delta E_{L,\beta}$ with $\pm 0.5\Delta E_{L,\beta}$ as the uncertainty. For $L>1$, the values are $\Delta E_{L,\beta}$ with $\pm 1.5\Delta E_{L,\beta}\langle x^{-6}\rangle_{nL}/\langle x^{-4}\rangle_{nL}$ as an estimate of the contribution from higher-order terms [cf. Eq (8)].

The complete asymptotic expression for $\Delta E_{L,1}$ is

$$\Delta E_{L,1}=\frac{4\alpha^3 Z}{3\pi}\Bigg\{\left(Z^3-\tfrac{31}{2}Z^{-3}\langle x^{-4}\rangle_{nL}+\tfrac{1447}{16}Z^{-5}\langle x^{-6}\rangle_{nL}\right)$$
$$\times\left[\ln(Z\alpha)^{-2}+\tfrac{19}{30}-\beta_{1s}-\left(\frac{Z-1}{Z}\right)^4 n^{-3}\beta_{nL}-0.31626Z^{-6}\langle x^{-4}\rangle_{nL}+2.296\pi\alpha Z+\frac{\mu}{M}C_M\right]\Bigg\}-\Delta E_L(1s)\,. \tag{16}$$

For arbitrary Z, $\langle x^{-4}\rangle_{nL}$ scales as $(Z-1)^4$. Numerical values obtained from Eq. (1) and Eq. (16) are compared in Table II. The differences are due entirely to the use of the asymptotic expansion for $\pi\langle\delta(\mathbf{r}_1)+\delta(\mathbf{r}_2)\rangle$ in Eq. (16) (represented by the first group of terms in parentheses), in place of the exact values [10]. For $L\geq 4$, the results become practically indistinguishable. The above does not include the Araki-Sucher electron-electron QED terms denoted in previous work [1,2] as $\Delta E_{L,2}$. These have already been calculated to high accuracy. The asymptotic form is

$$\Delta E_{L,2}=-\frac{7\alpha^3}{6\pi}\left(\langle x^{-3}\rangle_{nL}+3Z^{-2}\langle x^{-5}\rangle_{nL}\right)\,. \tag{17}$$

The second term comes from a multipole expansion of $1/r_{12}^3$. Also not included are spin-dependent anomalous magnetic moment corrections which spin average to zero.

An interpretation of these results is that the study of transition energies among the Rydberg states of helium probes the effects of electric fields on the Lamb shift of $\mathrm{He}^+(1s)$ through the $\langle x^{-4}\rangle_{nL}$ terms in Eq. (16). Almost all of $\Delta E_{L,1}$ can be interpreted in this way, with the larger part coming from the polarization of the $\pi\langle\delta(\mathbf{r}_1)+\delta(\mathbf{r}_2)\rangle$ electron density at the nucleus, and the smaller part from $\Delta E_{L,\beta}$ in Table II. The remainder comes from the small β_{nL} Bethe logarithm term in Eq. (16) for the Rydberg electron [9]. The overall agreement between theory and experiment for the low-lying states is satisfactory at the ± 1 MHz level [2], but for transitions among the $n=10$ states, there are important discrepancies between theory and the revised experimental data of Hessels *et al.* [3] as shown in Table III. The spin-averaged transition energies are nearly independent of spin-dependent effects. With the addition of the $\Delta E_{L,\beta}$ contribution, the theoretical values are the same as published previously [1]. The differences are several times larger than the residual Casimir-Polder retardation corrections V''_{ret} tabulated by Au and Mesa [6], which are shown separately in Table III. The last column gives the contributions from the screened one-electron Dirac energies $\Delta E_D^{(4)}$ of order $\alpha^4(Z-1)^6$. Since these are also much too small, and other sources of theoretical uncertainty have now been reduced, there appears to be a well-defined systematic discrepancy between theory and experiment. The discrepan-

TABLE II. Values for the energy shifts $\Delta E_{L,\beta}$ and $\Delta E_{L,1}$, in MHz. The last two columns compare Eq. (1) with the asymptotic Eq. (16).

State	$\Delta E_{L,\beta}$	$\Delta E_{L,1}$ [Eq. (1)]	$\Delta E_{L,1}$ [Eq. (16)]
2^1P	−1.8(1.8)[a]	101.2(1.8)	−1087.4
2^3P	−1.8(1.8)	−1213.1(1.8)	−1087.4
3^1P	−0.6(6)	34.2(6)	−357.8
3^3P	−0.6(6)	−346.9(6)	−357.8
3^1D	−0.047(17)	−11.63(2)	−9.53
3^3D	−0.047(17)	−14.36(2)	−9.53
10^1D	−0.0016(8)	−0.366(1)	−0.255
10^3D	−0.0016(8)	−0.492(1)	−0.255
10^1F	−0.00026(1)	−0.0736(1)	−0.0727
10^3F	−0.00026(1)	−0.0746(1)	−0.0727
$10G$	−0.000069(1)	−0.01950(1)	−0.01950
$10H$	−0.000024(0)	−0.00659	−0.00660
$10I$	−0.000010(0)	−0.00262	−0.00262
$10K$	−0.000005(0)	−0.00116	−0.00116

[a] Numbers in parentheses denote uncertainties in the final figures quoted.

TABLE III. Comparison of theory and experiment for the spin-averaged transition frequencies among the $n=10$ states of helium (in MHz).

Transition	Experiment	Theory	Difference	$\Delta V''_{\mathrm{rel}}$ [a]	$\Delta E_D^{(4)}$
D-F	14560.651(34) [b]	14560.655(1)	0.004(35)	−0.002397	0.000153
F-G	2036.5588(22) [c]	2036.5745(1)	−0.0157(23)	−0.001223	0.000046
G-H	491.0052(5) [c]	491.0083(1)	−0.0031(6)	−0.000714	0.000018
H-I	157.0524(2) [c]	157.0537(0)	−0.0013(2)	−0.000453	0.000009
I-K	60.8160(2) [c]	60.8168(0)	−0.0008(2)	−0.000304	0.000004

[a] Au and Mesa (Ref. [6]).

[b] Farley, MacAdam, and Wing (Ref. [12]) global fit.

[c] Hessels *et al.* (Ref. [3]).

cies for the higher-L transitions would be removed by an additional energy term of $\sim 2.4\alpha^3\langle x^{-4}\rangle_{nL}$ a.u. However, this would shift the 10D-10F transition by about −100 kHz. Since this is the one case that appears to agree with theory, but with lower accuracy, a repetition of the measurement could be significant in confirming or resolving the disagreement. The above additional term would also seriously disrupt the existing agreement between theory and experiment for transitions among the lower-lying states, as fully discussed in Ref. [2].

Research support by the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged. One of us (G.W.F.D.) wishes to thank the Killam Foundation for support.

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