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Higher-order relativistic corrections to the polarization energies of helium Rydberg states

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Accurate energies of helium Rydberg states have been obtained by Drachman using polarization potentials [Phys. Rev. A **26**, 1228 (1982); **31**, 1253 (1985); **38**, 1659(E) (1988)]. The present work calculates the higher-order relativistic corrections up to order $\alpha^2\langle(a_0/r_2)^6\rangle e^2/a_0$, where $\mathbf{r}_2$ is the position of the Rydberg electron. The results given simple formulas for these contributions, which can easily be evaluated for any Rydberg state. The results are compared (at lower L) to precise variational calculations, and are compared to recent precisely measured $n=10$ intervals.

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INTRODUCTION

Calculations of the energies of high-angular-momentum Rydberg states of helium have advanced greatly in the past decade. In 1982, Drachman published [1] calculations in which the energies could be expressed in terms of simple long-range polarization potentials. In 1985, after improved measurements [2] of these states, the lowest-order relativistic corrections to the polarization potentials were calculated [3]. In 1990, variational energies for states up to 10K ($n=10, l=7$) were calculated [4], giving very accurate eigenvalues for these states. Recent higher-precision measurements [5] in $n=10$ states of helium make it desirable to calculate higher-order relativistic corrections to the polarization potentials. These relativistic corrections are calculated here and shown to be simple expressions that can easily be evaluated for any nl Rydberg state. The corrections are compared to the variational calculations at lower l, and are compared to experiment in $n=10$. In this work, all spin-independent relativistic effects to order $\alpha^2\ \langle(a_0/r_2)^6\rangle$ are included.

In the next section, a brief review of the nonrelativistic polarization potential is presented. In the following section, the higher-order relativistic calculations are presented. Finally, the calculations are compared to experiment for $n=10$ intervals.

NONRELATIVISTIC POLARIZATION POTENTIAL

The nonrelativistic Hamiltonian

$$H_{\mathrm{nr}}=\frac{p_1^2}{2m}+\frac{p_2^2}{2m}-\frac{2e^2}{r_1}-\frac{2e^2}{r_2}+\frac{e^2}{r_{12}} \tag{1}$$

can be separated into

$$H_{\mathrm{nr}}=H_{0c}+H_{0r}+V\ , \tag{2}$$

where

$$H_{0c}=\frac{p_1^2}{2m}-\frac{2e^2}{r_1}\ , \tag{3}$$

$$H_{0r}=\frac{p_2^2}{2m}-\frac{e^2}{r_2}\ , \tag{4}$$

and

$$V=\frac{e^2}{r_{12}}-\frac{e^2}{r_2}=e^2\left[\sum_{k=0}^{\infty}\frac{r_<^k}{r_>^{k+1}}P_k(\hat{\mathbf{r}}_1\cdot\hat{\mathbf{r}}_2)-\frac{1}{r_2}\right]\ , \tag{5}$$

where $r_>$ ($r_<$) is the larger (smaller) of r_1 and r_2 and P_k is a Legendre polynomial. H_{0c} is a $Z=2$ hydrogenic Hamiltonian for the inner (core) electron and H_{0r} is a $Z=1$ hydrogenic Hamiltonian for the outer (Rydberg) electron. The fact that $H_0=H_{0c}+H_{0r}$ is not symmetric under the interchange of $\mathbf{r}_1$ and $\mathbf{r}_2$ implies that one must use unsymmetric perturbation theory [6] instead of the usual Raleigh-Schrödinger perturbation theory. For high-L Rydberg states, the core and Rydberg electrons occupy different regions of space, since the outer electron is excluded from positions near the nucleus by its centrifical potential. For example, for the hydrogenic $(1S)(10M)$ state ($n=10, L=9$), the inner electron has a probability of less than 10^{-14} of being outside $10a_0$, while the outer electron has a probability of only 10^{-14} of being inside $10a_0$. Because the wave functions of the two electrons do not overlap, it is possible to disregard symmetrization, and treat the electrons as distinct.

The potential V can be written (in atomic units) as

$$V=\sum_{k=1}^{\infty}V_c^{(k)}+\sum_{k=0}^{\infty}V_s^{(k)}\ , \tag{6}$$

where

$$V_c^{(k)}=\frac{r_1^k}{r_2^{k+1}}P_k(\hat{\mathbf{r}}_1\cdot\hat{\mathbf{r}}_2) \tag{7}$$

and

$$V_s^{(k)}=\begin{cases}\left[\dfrac{r_2^k}{r_1^{k+1}}-\dfrac{r_1^k}{r_2^{k+1}}\right]P_k(\hat{\mathbf{r}}_1\cdot\hat{\mathbf{r}}_2) & \text{for } r_1>r_2\\ 0 \quad \text{for } r_1<r_2\ . \end{cases} \tag{8}$$

The zeroth-order energies are $E^{(0)}=-2-1/2n^2$, and the zeroth-order wave functions are

$$\psi_0(\mathbf{r}_1,\mathbf{r}_2)=|(1s)(nl)\rangle=\psi_{1s}^{Z=2}(\mathbf{r}_1)\psi_{nl}^{Z=1}(\mathbf{r}_2)\ . \tag{9}$$

The higher-order energies are obtained from perturbation theory, $E=E^{(0)}+E^{(1)}+E^{(2)}+\dots$, where

$$E^{(1)}=\langle (1s)(nl)|V|(1s)(nl)\rangle \;, \tag{10}$$

$$E^{(2)}=\sum_{N,L,n',l'} \frac{|\langle (1s)(nl)|V|(NL)(n'l')\rangle|^2}{E_{1snl}-E_{NLn'l'}} \;, \tag{11}$$

$$E^{(3)}=\sum_{\substack{N,LN',L',\\ n'l',n'',l''}} \frac{\langle (1s)(nl)|V|(NL)(n'l')\rangle\langle (NL)(n'l')|V|(N'L')(n''l'')\rangle\langle (N'L')(n''l'')|V|(1s)(nl)\rangle}{(E_{1snl}-E_{NLn'l'})(E_{1snl}-E_{N'L'n''l''})}$$

$$-\langle (1s)(nl)|V|(1s)(nl)\rangle \sum_{N,L,n'l'} \frac{|\langle (1s)(nl)|V|(NL)(n'l')\rangle|^2}{(E_{1snl}-E_{NLn'l'})^2} \;. \tag{12}$$

Here the sums are assumed to include the continuum and to exclude the $(1s)(nl)$ state. The energy denominators can be expanded as

$$(E_{1snl}-E_{NLn'l'})=(E_{1s}-E_{NL})^{-1}+(E_{n'l'}-E_{nl})(E_{1s}-E_{NL})^{-2}+\dots \;, \tag{13}$$

with the first term giving the adiabatic energies, the next term the first nonadiabatic corrections, etc. Using these expansions, the most significant terms of V_c have been evaluated analytically [1]:

$$E=E^{(0)}-\frac{\alpha_1}{2}\left\langle\frac{1}{r_2^4}\right\rangle_{nl}+\left[-\frac{\alpha_2}{2}+3\beta_1\right]\left\langle\frac{1}{r_2^6}\right\rangle_{nl}+\dots \;, \tag{14}$$

where $\alpha_1=\frac{9}{32}$ is the dipole polarizability of He^+, $\alpha_2=\frac{15}{64}$ is the quadrupole polarizability, and $\beta_1=\frac{43}{512}$ is the nonadiabatic correction to the dipole polarizability. The notation $\langle r_2^{-k}\rangle_{nl}$ refers to the hydrogenic expectation value, and all terms up to order $\langle r_2^{-8}\rangle$ have were included by Drachman [1,7] and terms up to $\langle r_2^{-10}\rangle$ have recently been calculated [8]. Since $\langle r_2^{-k}\rangle$ decreases quickly with k for high-L Rydberg states, only relativistic corrections of the terms up to order $\langle r_2^{-6}\rangle$ are included in the present calculations.

The $V_s^{(k)}$ part of the Coulomb perturbation gives a first-order contribution of

$$-\sum_{j,k=0}^{n-l-1}\frac{(n-l-1)!(n+l)!(-2/n)^{2l+j+k+2}/n^2}{k!j!(n-l-1-k)!(n-l-1-j)!(2l+1+j)!(2l+1+k)!}\left[\frac{2(2l+j+k+2)!}{(4+2/n)^{2l+j+k+3}}+\frac{(2l+j+k+1)!}{(4+2/n)^{2l+j+k+2}}\right] . \tag{15}$$

These contributions are very small (less than 100 Hz for $l>4$ and less than 0.1 Hz for $l>5$). Similar contributions from second-order perturbation theory due to $V_s^{(k)}$ times $V_c^{(k)}$ are similarly small. Thus, only the relativistic corrections of the potentials that result from the $V_c^{(k)}$ perturbations are included in the present calculations.

RELATIVISTIC CORRECTIONS

The goal of the present work is to obtain all relativistic corrections to the polarizabilities up to order $\alpha^2\langle r_2^{-6}\rangle$ (where α is the fine-structure constant). The relativistic corrections to the Hamiltonian H_0 are given (in atomic units) by [6]

$$H_{\rm rel}=H_1+H_2+H_4 \;, \tag{16}$$

where

$$H_1=H_{1C}+H_{1R}=-\tfrac{1}{8}\alpha^2p_1^4-\tfrac{1}{8}\alpha^2p_2^4 \tag{17}$$

are the relativistic corrections to the kinetic energy of the core and Rydberg electrons,

$$H_2=-\tfrac{1}{2}\alpha^2\frac{1}{r_{12}}[\mathbf{p}_1\cdot\mathbf{p}_2+\hat{\mathbf{r}}_{12}\cdot(\hat{\mathbf{r}}_{12}\cdot\mathbf{p}_1)\mathbf{p}_2] \tag{18}$$

is the relativistic retardation correction, and

$$H_4=\pi\alpha^2\delta^{(3)}(\mathbf{r}_1) \tag{19}$$

is the Darwin term. The Hamiltonians H_3 and H_5, which give the spin structure, have been ignored, since we will consider only the spin-independent structure. H_3 and H_5 have been treated elsewhere in long-range hydrogenic models [9–11]. Also, terms proportional to $\delta(\mathbf{r}_{12})$ and $\delta(\mathbf{r}_2)$ have been ignored, since high-L Rydberg electrons do not penetrate into the core.

The effects of H_{1C} and H_4 on the dipole polarizability (α_1) come from third-order energies involving $V_c^{(1)}$, $V_c^{(1)}$, and $(H_{1C}+H_4)$ and have been calculated previously [3] to be

$$\tfrac{1936}{768}\alpha^2\left\langle\frac{1}{r_2^4}\right\rangle-\tfrac{31}{16}\alpha^2\left\langle\frac{1}{r_2^4}\right\rangle=\tfrac{7}{12}\alpha^2\left\langle\frac{1}{r_2^4}\right\rangle . \tag{20}$$

The effects of H_{1C} and H_4 on the quadrupole polarizability were also calculated [3]:

$$\tfrac{229}{80}\alpha^2\left\langle\frac{1}{r_2^6}\right\rangle+\tfrac{-557}{256}\alpha^2\left\langle\frac{1}{r_2^6}\right\rangle=\tfrac{879}{1280}\alpha^2\left\langle\frac{1}{r_2^6}\right\rangle . \tag{21}$$

A third term, also proportional to r_2^{-6}, comes from the relativistic corrections to the nonadiabatic dipole polarizability (β_1). This term has not been previously calculated and is necessary in order to make precise comparisons between theory and recent experiments.

The term comes from the third-order energy. Taking the first nonadiabatic corrections to the energy denominators of Eq. (12) gives

$$-2\sum_{\substack{N,L,\\N',L',n',l'}}\frac{\langle 1s|H_{1c}+H_4|NL\rangle\langle (NL)(nl)|V_c^{(1)}|(N'L')(n'l')\rangle\langle (N'L')(n'l')|V_c^{(1)}|(1s)(nl)\rangle(E_{nl}-E_{n'l'})}{(E_{1s}-E_{NL})(E_{1s}-E_{N'L'})^2}$$

$$-2\sum_{\substack{N,L,\\N',L',n',l'}}\frac{\langle (1s)(nl)|V_c^{(1)}|(NL)(n'l')\rangle\langle NL|H_{1c}+H_4|N'L'\rangle\langle (N'L')(n'l')|V_c^{(1)}|(1s)(nl)\rangle(E_{nl}-E_{n'l'})}{(E_{1s}-E_{NL})^2(E_{1s}-E_{N'L'})}$$

$$+2\sum_{\substack{N,L,\\n',l'}}\langle 1s|H_{1c}+H_4|1s\rangle\frac{|\langle (1s)(nl)|V_c^{(1)}|(NL)(n'l')\rangle|^2}{(E_{1s}-E_{NL})^3}(E_{nl}-E_{n'l'})\ . \tag{22}$$

The first term can be simplified using

$$[H_{0c}(\mathbf{r}_1),[H_{0c}(\mathbf{r}_1),F^{(1)}]]|1s\rangle=V_c^{(1)}|1s\rangle \tag{23}$$

for

$$F^{(1)}=\frac{\hat{\mathbf{r}}_1\cdot\hat{\mathbf{r}}_2}{r_2^2}\left(\tfrac{11}{96}r_1+\tfrac{11}{96}r_1^2+\tfrac{1}{24}r_1^3\right)\ . \tag{24}$$

The term then reduces to

$$2\sum_{\substack{N,L,\\N',L',n',l'}}\frac{\langle 1s|H_{1c}+H_4|NL\rangle\langle (NL)(nl)|H_{0r}(\mathbf{r}_2)V_c^{(1)}-V_c^{(1)}H_{0r}(\mathbf{r}_2)|(N'L')(n'l')\rangle}{E_{1s}-E_{NL}}$$

$$\times\left\langle (N'L')(n'l')\left|\frac{\hat{\mathbf{r}}_1\cdot\hat{\mathbf{r}}_2}{r_2^2}\left[\frac{11}{96}r_1+\frac{11}{96}r_1^2+\frac{1}{24}r_1^3\right]\right|(1s)(nl)\right\rangle\ , \tag{25}$$

where the E_n-E_n' factor is taken inside of the $V_c^{(1)}$ matrix element. Using

$$[H_{0r}(\mathbf{r}_2),V_c^{(1)}]|nl\rangle=\frac{2r_1}{r_2^3}\hat{\mathbf{r}}_1\cdot\hat{\mathbf{r}}_2\frac{\partial}{\partial r_2}-\frac{r_1}{r_2^4}\frac{\partial P_1(\cos\theta_{12})}{\partial\theta_2}\frac{\partial}{\partial\theta}|nl\rangle \tag{26}$$

and noting that the expectation value of the second term is zero and using the completeness of $|n'l'\rangle$, Eq. (25) reduces to

$$2\sum_{N,L}\frac{\langle 1s|H_{1c}+H_4|NL\rangle}{E_{1s}-E_{NL}}\left\langle (1s)(nl)\left|\frac{\hat{\mathbf{r}}_1\cdot\hat{\mathbf{r}}_2}{r_2^2}\left[\frac{11}{96}r_1+\frac{11}{96}r_1^2+\frac{1}{24}r_1^3\right]\frac{2r_1}{r_2^3}\hat{\mathbf{r}}_1\cdot\hat{\mathbf{r}}_2\frac{\partial}{\partial r_2}\right|(NL)(nl)\right\rangle\ . \tag{27}$$

Since $V_{\rm rel}$ is a scalar operator, $|NL\rangle$ is restricted to s states, and only the scalar part of $(\hat{\mathbf{r}}_1\cdot\hat{\mathbf{r}}_2)(\hat{\mathbf{r}}_1\cdot\hat{\mathbf{r}}_2)$ (which equals $\frac{1}{3}$) will contribute. Noting that

$$[H_{0c}(\mathbf{r}_1),\tfrac{11}{96}r_1^2+\tfrac{11}{96}r_1^3+\tfrac{1}{24}r_1^4]|1s\rangle$$
$$=\tfrac{1}{96}\left(\tfrac{2}{5}r_1^5+\tfrac{17}{8}r_1^4+\tfrac{43}{8}r_1^3+\tfrac{129}{16}r_1^2-\tfrac{3855}{256}\right)|1s\rangle \tag{28}$$

and that (using integration by parts) for $l>\frac{1}{2}(k-2)$

$$\left\langle nl\left|\frac{1}{r_2^k}\frac{\partial}{\partial r_2}\right|nl\right\rangle=\frac{k-2}{2}\left\langle nl\left|\frac{1}{r_2^{k+1}}\right|nl\right\rangle\ , \tag{29}$$

we obtain

$$-2\langle 1s|(H_{1c}+H_4)\tfrac{1}{96}\left(\tfrac{2}{5}r_1^5+\tfrac{17}{8}r_1^4+\tfrac{43}{8}r_1^3\right.$$
$$\left.+\tfrac{129}{16}r_1^2-\tfrac{3855}{256}\right)|1s\rangle\langle r_2^{-6}\rangle_{nl}\ . \tag{30}$$

This gives $-\frac{57}{16}\alpha^2\langle r_2^{-6}\rangle$ and $\frac{1285}{512}\alpha^2\langle r_2^{-6}\rangle$ for H_{1c} and H_4, respectively.

Calculation of the second and third terms of Eq. (22) is carried out in a similar fashion. The second term gives $\frac{551}{1536}\alpha^2\langle r_2^{-6}\rangle$ and zero for the H_{1c} and H_4 contributions, while the third term gives $-\frac{1595}{512}\alpha^2\langle r_2^{-6}\rangle$ and $\frac{319}{128}\alpha^2\langle r_2^{-6}\rangle$, respectively. Thus, the total contribution of the relativistic corrections to β_1 is

$$-\tfrac{2023}{1536}\alpha^2\langle r_2^{-6}\rangle\ . \tag{31}$$

The contributions of these relativistic corrections are listed in Table I in the column labeled $\alpha_2^{\rm rel}+\beta_1^{\rm rel}$.

Another term, the relativistic correction of the dipole polarizability due to H_{1R}, has contributions of similar size and must also be included. These corrections come from third-order perturbation-theory expressions [Eq. (12)] containing $V_c^{(1)}$, $V_c^{(1)}$, and H_{1R}. The term that contains $\langle (1s)(nl)|H_{1R}|(NL)(n'l')\rangle$ dominates, since it is nonzero only for $(NL)=(1s)$, and this leads to a small denominator: $E_{nl}-E_{n'l'}$. The exact solution to this term has recently been carried out by Drake [12], who obtained

TABLE I. Relativistic corrections to the polarization energies. The second column lists the relativistic corrections due to H_1+H_4 from the variational calculations of Drake [12]. The third column gives the lowest-order corrections as calculated by Drachman using his polarization model [3]. The next columns give the higher-order corrections due to $H_{1C}+H_4$ and H_{1R}, respectively. The next column lists the total of the previous three columns, which is the total of the corrections in the polarization model. The final column gives the difference between this polarization model prediction and the variational calculation. All values are in MHz, with error estimates in parentheses.

	Variational	$\alpha_1^{\rm rel}$	$\alpha_2^{\rm rel}+\beta_1^{\rm rel}$	$\Delta(H_{1R})$	Total	Difference
10*F*	+0.5501(3)	+0.6229	−0.0224	−0.0679	0.5326	0.0175(3)
10*G*	+0.155 05(0)	+0.165 16	−0.001 60	−0.008 99	0.154 57	0.000 48(0)
10*H*	+0.055 05(6)	+0.057 17	−0.000 21	−0.001 91	0.055 05	0.000 00(6)
10*I*	+0.022 868(9)	+0.023 413	−0.000 037	−0.000 515	0.022 861	0.000 007(9)
10*K*	+0.010 580(3)	+0.010 746	−0.000 008	−0.000 159	0.010 579	0.000 001(3)
10*L*		+0.005 343	−0.000 002	−0.000 053	0.005 288	
10*M*		+0.002 812	−0.000 001	−0.000 018	0.002 793	

$$\Delta\alpha_1(H_{1r})=\alpha^2\frac{9}{32}\left[\left[\frac{3}{2n^2}-\sum_{j=2l-1}^{2l+3}\frac{1}{j(2l+1)}-\frac{9n-5l(l+1)/n+2l+1}{2(2l+1)[3n^2-l(l+1)]}\right]\times\langle r_2^{-4}\rangle-\tfrac{1}{2}\langle r_2^{-5}\rangle\right]. \quad (32)$$

I have calculated the other terms in the third-order energy [Eq. (12)]. These terms contribute

$$-\frac{43\alpha^2}{1024}\{\tfrac{1}{16}\langle r_2^{-6}\rangle+[\tfrac{33}{40}-\tfrac{17}{80}l(l+1)]\langle r_2^{-7}\rangle+[-\tfrac{111}{8}-\tfrac{1}{5}l(l+1)+\tfrac{2}{5}l^2(l+1)^2]\langle r_2^{-8}\rangle\} \quad (33)$$

and

$$\frac{43\alpha^2}{1024n^3}\left[-\frac{3}{4n}+\frac{1}{l+\frac{1}{2}}\right]\langle r_2^{-4}\rangle . \quad (34)$$

Inclusion of these terms is necessary to get all contributions of order $\alpha^2\langle r_2^{-6}\rangle$, but evaluation of these terms indicates that their contribution is small. The energies from these contributions are included in Table I. These results complete all of the H_1+H_4 corrections up to order $\alpha^2\langle r_2^{-6}\rangle$.

A comparison between the relativistic effects of H_1+H_4 as calculated by Drake using variational wave functions [4,12], and as calculated here in terms of corrections to the polarizabilities, is given in Table I. In the second column the variational calculations of Drake for $n=10$ are given (with the first-order energies $\langle H_1+H_4\rangle$ subtracted out). The sixth column gives the total of the corrections to α_1, α_2, and β_1 due to $H_{1c}+H_4$ and of α_1 due to H_{1R}. The final column gives the differences, which go very quickly to zero as L increases. For the higher-L states, where the variational wave functions are not available, the polarization model predictions are reliable at the Hz level of accuracy. Thus, the effects of H_1+H_4 are approximated well by

$$\frac{\alpha^2}{2n^3}\left[\frac{-1}{l+\frac{1}{2}}+\frac{3}{4n}-\frac{m_e}{M_\alpha}\left[\frac{1}{n}-\frac{1}{l+\frac{1}{2}}\right]\right]+\tfrac{7}{12}\alpha^2\left\langle\frac{1}{r_2^4}\right\rangle_{nl}-\tfrac{4841}{7680}\alpha^2\langle r_2^{-6}\rangle_{nl}+\Delta(H_{1R}) , \quad (35)$$

where the first term is simply the expectation value of H_{1R} (with appropriate mass corrections [13]), $\Delta(H_{1R})$ is the sum of Eqs. (32)–(34), and the other terms are corrections to the polarizabilities due to $H_{1C}+H_4$ as discussed above.

We now consider H_2, which leads to retardation corrections. The lowest-order retardation contribution is known to be $\alpha^2\langle r_2^{-4}\rangle/4$ [14]. A derivation of this result from H_2 and $V_c^{(1)}$ within the present formalism is given below. It is then extended to obtain new corrections due to H_2 or oder $\alpha^2\langle r_2^{-6}\rangle$ to the polarization energies.

The operator

$$H_2=-\tfrac{1}{2}\alpha^2\frac{1}{r_{12}}[\mathbf{p}_1\cdot\mathbf{p}_2+\hat{\mathbf{r}}_{12}\cdot(\hat{\mathbf{r}}_{12}\cdot\mathbf{p}_1)\mathbf{p}_2)] \quad (36)$$

can be expanded in terms of powers of r_1/r_2 to obtain

$$H_2=H_2^{(1)}+H_2^{(2)}+H_2^{(3)}+\ldots , \quad (37)$$

where

$$H_2^{(1)}=-\tfrac{1}{2}\alpha^2\frac{1}{r_2}[\mathbf{p}_1\cdot\mathbf{p}_2+\hat{\mathbf{r}}_2\cdot(\hat{\mathbf{r}}_2\cdot\mathbf{p}_1)\mathbf{p}_2] , \quad (38)$$

$$H_2^{(2)}=-\tfrac{1}{2}\alpha^2\frac{r_1}{r_2^2}[\hat{\mathbf{r}}_1\cdot\hat{\mathbf{r}}_2\mathbf{p}_1\cdot\mathbf{p}_2+3\hat{\mathbf{r}}_1\cdot\hat{\mathbf{r}}_2\hat{\mathbf{r}}_2\cdot(\hat{\mathbf{r}}_2\cdot\mathbf{p}_1)\mathbf{p}_2-\hat{\mathbf{r}}_1\cdot(\hat{\mathbf{r}}_2\cdot\mathbf{p}_1)\mathbf{p}_2-\hat{\mathbf{r}}_2\cdot(\hat{\mathbf{r}}_1\cdot\mathbf{p}_1)\mathbf{p}_2] , \quad (39)$$

and

$$H_2^{(3)}=-\tfrac{1}{2}\alpha^2\frac{r_1^2}{r_2^3}\{(\tfrac{3}{2}\hat{\mathbf{r}}_1\cdot\hat{\mathbf{r}}_2\hat{\mathbf{r}}_1\cdot\hat{\mathbf{r}}_2-\tfrac{1}{2})[\mathbf{p}_1\cdot\mathbf{p}_2+3\hat{\mathbf{r}}_2\cdot(\hat{\mathbf{r}}_2\cdot\mathbf{p}_1)\mathbf{p}_2]+3\hat{\mathbf{r}}_1\cdot\hat{\mathbf{r}}_2\hat{\mathbf{r}}_1\cdot\hat{\mathbf{r}}_2\hat{\mathbf{r}}_2\cdot(\hat{\mathbf{r}}_2\cdot\mathbf{p}_1)\mathbf{p}_2-3\hat{\mathbf{r}}_1\cdot\hat{\mathbf{r}}_2\hat{\mathbf{r}}_1\cdot(\hat{\mathbf{r}}_2\cdot\mathbf{p}_1)\mathbf{p}_2+\hat{\mathbf{r}}_1\cdot(\hat{\mathbf{r}}_1\cdot\mathbf{p}_1)\mathbf{p}_2\} . \quad (40)$$

The lowest-order contribution of H_2 to the helium Rydberg energy levels comes from the second-order perturbation between $H_2^{(1)}$ and $V_c^{(1)}$, which gives

$$2\sum_{N,L,n',l'} \frac{\left\langle (1s)(nl)\left|\frac{r_1}{r_2^2}\hat{\mathbf{r}}_1\cdot\hat{\mathbf{r}}_2\right|(NL)(n'l')\right\rangle\left\langle (NL)(n'l')\left|-\tfrac{1}{2}\alpha^2\frac{1}{r_2}[\mathbf{p}_1\cdot\mathbf{p}_2+\hat{\mathbf{r}}_2\cdot(\hat{\mathbf{r}}_2\cdot\mathbf{p}_1)\mathbf{p}_2]\right|(1s)(nl)\right\rangle}{E_{1s}-E_{NL}} . \quad (41)$$

Using

$$G^{(1)}=\frac{1}{4}\frac{r_1+r_1^2}{r_2^2}\hat{\mathbf{r}}_1\cdot\hat{\mathbf{r}}_2 , \quad (42)$$

which satisfies

$$[H_{0c}(\mathbf{r}_1),G^{(1)}]|1s\rangle=\frac{r_1}{r_2^2}\hat{\mathbf{r}}_1\cdot\hat{\mathbf{r}}_2|1s\rangle , \quad (43)$$

and using the fact that

$$\nabla_1\psi_{1s}=-2\hat{\mathbf{r}}_1\psi_{1s} , \quad (44)$$

along with

$$\hat{\mathbf{r}}_2\cdot\nabla_2=\frac{\partial}{\partial r_2} , \quad (45)$$

Eq. (41) reduces to

$$2\left\langle (1s)(nl)\left|-\frac{1}{4}\frac{r_1+r_1^2}{r_2^2}\hat{\mathbf{r}}_1\cdot\hat{\mathbf{r}}_2(-\tfrac{1}{2}\alpha^2)\frac{1}{r_2}(2)\left[\hat{\mathbf{r}}_1\cdot\nabla_2+\hat{\mathbf{r}}_1\cdot\hat{\mathbf{r}}_2\frac{\partial}{\partial r_2}\right]\right|(1s)(nl)\right\rangle . \quad (46)$$

Since we need the expectations value between $1s$ states, only the scalar part of the operator survives. Since the scalar part of $\hat{\mathbf{r}}_1\cdot\mathbf{A}(\mathbf{r}_2)\hat{\mathbf{r}}_1\cdot\mathbf{B}(\mathbf{r}_2)$ is $\frac{1}{3}\mathbf{A}(\mathbf{r}_2)\cdot\mathbf{B}(\mathbf{r}_2)$, the expression reduces to

$$\tfrac{1}{2}\alpha^2\langle 1s|r_1+r_1^2|1s\rangle\tfrac{1}{3}\left\langle nl\left|\frac{2}{r_2^3}\frac{\partial}{\partial r_2}\right|nl\right\rangle=\tfrac{1}{4}\alpha^2\langle r_2^{-4}\rangle_{nl} . \quad (47)$$

This is the lowest-order approximation to the dipole retardation correction. The full dipole retardation contribution has been discussed at length [14–16]. Precise calculations of the dipole contributions have been done and the results for a wide range of states have been tabulated [16,17]. For short distances the full dipole retardation contributions can be approximated [16] by $\langle V_{\rm ret}\rangle_{nl}$, where

$$V_{\rm ret}=\tfrac{1}{4}\alpha^2 r_2^{-4}-\frac{7}{6\pi}\alpha^3 r_2^{-3}+\tfrac{4}{3}\alpha^4 r_2^{-2}+\dots . \quad (48)$$

This potential includes effects other than H_2, with the r^{-3} term, for example, coming from the two-electron Lamb shift [4,15]. Since the H_2 contribution is the largest portion of the dipole retardation potential, the higher-order effects of the H_2 part of the retardation potential will be calculated. The terms that give results proportional to $\alpha^2\langle r_2^{-6}\rangle$ are the second-order perturbation terms: $H_2^{(1)}V_c^{(3)}$, $H_2^{(3)}V_c^{(1)}$, $H_2^{(2)}V_c^{(2)}$, and the nonadiabatic correction to $H_2^{(1)}V_c^{(1)}$. The first three of these are calculated using methods similar to those used for $H_2^{(1)}V_c^{(1)}$. The results are 0, $\frac{-15}{64}\alpha^2\langle r_2^{-6}\rangle$, and $\frac{27}{64}\alpha^2\langle r_2^{-6}\rangle$, respectively. The nonadiabatic term is

$$2\sum_{\substack{N,L,\\ n',l'}}\frac{\langle (1s)(nl)|V_c^{(1)}|(NL)(n'l')\rangle\langle (NL)(n'l')|H_2^{(1)}|(1s)(nl)\rangle}{(E_{1s}-E_{NL})^2}(E_{n'l'}-E_{nl}) . \quad (49)$$

The operator $F^{(1)}$ of Eq. (24) can be used to cancel the energy denominators, and putting the factor $E_{n'l'}-E_{nl}$ inside of the first matrix element and using Eq. (26), we obtain

$$-\alpha^2\left\langle 1s\left|(\tfrac{11}{96}r_1+\tfrac{11}{96}r_1^2+\tfrac{1}{24}r_1^3)\left[\left\langle\frac{\partial}{\partial r_2}\psi_{nl}\right|\frac{2\hat{\mathbf{r}}_1\cdot\hat{\mathbf{r}}_2}{r_2^3}-\left\langle\frac{\partial}{\partial\theta_2}\psi_{nl}\right|\frac{\left[\frac{\partial}{\partial\theta_2}\hat{\mathbf{r}}_2\cdot\hat{\mathbf{r}}_2\right]}{r_2^4}\right]\frac{1}{r_2}\left[2\hat{\mathbf{r}}_1\cdot\nabla_2+2\hat{\mathbf{r}}_2\cdot\hat{\mathbf{r}}_1\frac{\partial}{\partial r_2}\right]\right|(1s)(nl)\right\rangle . \quad (50)$$

Here we have also used Eqs. (44) and (45) and the completeness of the $|n'l'\rangle$'s. Using the facts that $(\partial/\partial\theta_2)\hat{\mathbf{r}}_2=\hat{\boldsymbol{\theta}}_2$, $\hat{\boldsymbol{\theta}}_2\cdot\nabla_2=(1/r_2)(\partial/\partial\theta_2)$, and the two matrix elements

$$\left\langle \frac{\partial}{\partial r}\psi_{nl}\left|\frac{1}{r_2^4}\right|\frac{\partial}{\partial r}\psi_{nl}\right\rangle=[1+\tfrac{1}{3}l(l+1)]\langle r^{-6}\rangle-\tfrac{1}{3}\langle r_2^{-5}\rangle \tag{51}$$

and

$$\left\langle \frac{\partial}{\partial \theta}\psi_{nl}\left|\frac{1}{r_2^6}\right|\frac{\partial}{\partial \theta}\psi_{nl}\right\rangle=l(l+1)\langle r_2^{-6}\rangle\ , \tag{52}$$

Eq. (50) reduces to

$$\alpha^2[-\tfrac{9}{16}\langle r_2^{-6}\rangle-\tfrac{3}{64}l(l+1)\langle r_2^{-6}\rangle+\tfrac{3}{16}\langle r_2^{-5}\rangle]\ . \tag{53}$$

This, combined with the earlier terms, gives the total correction due to H_2 (to order $\alpha^2\langle r_2^{-6}\rangle$):

$$\tfrac{1}{4}\alpha^2\langle r_2^{-4}\rangle+\tfrac{3}{16}\alpha^2\langle r_2^{-5}\rangle-[\tfrac{3}{8}+\tfrac{3}{64}l(l+1)]\alpha^2\langle r_2^{-6}\rangle\ . \tag{54}$$

A comparison between the $n=10$ values from this expression and the H_2 corrections from Drake's variational calculations is given in Table II. The level of agreement is very high and increases rapidly with increasing L. For the higher-L states, where variational wave functions are not available, Eq. (54) appears to give values that are accurate to 1 Hz.

It should be noted that higher-order retardation effects have been discussed elsewhere. The retardation correction to β_1 was discussed in Ref. [18], but was not calculated. The leading-order term of the "electric quadrupole retardation effect" was calculated in Ref. [19] to be $\frac{9}{16}\alpha^2\langle r_2^{-6}\rangle_{nl}$, which differs from the present result. The calculation of Ref. [19] included the full retardation contributions (not just H_2). From the comparison with Drake's variational calculations, it is clear that Eq. (54) contains all of the H_2 corrections to order $\alpha^2\langle r_2^{-6}\rangle$. The size of the order $\alpha^2\langle r_2^{-6}\rangle$ retardation corrections not included in H_2 is a matter that warrants further investigation.

COMPARISON TO EXPERIMENT

Table III shows a comparison of experiment to both the variational calculations of Drake and the long-range calculations discussed above. The first row gives the experimental results for measurements of $n=10$ intervals [5,20]. The second row gives the nonrelativistic contributions to these intervals as calculated by Drake [4], the third row is the difference between the first and second rows and is thus the net relativistic and radiative contributions to these intervals. These contributions are compared to variational calculations and long-range calculations of the lower sections of the table. The variational calculations of Drake [4] include relativistic corrections from the Breit interaction (H_1, H_2, and H_4) as well as one- and two-electron Lamb shifts (L_1,L_2)[21]. The $V''_{\rm ret}$ term, as discussed by Au [15] and Drake [4], is a correction to Drake's calculation which includes retardation effects not included in H_2 or the two-electron Lamb shift. The total contributions of relativistic and radiative effects to the $n=10$ intervals as calculated using variational methods are shown in the tenth row of Table III and are several standard deviations larger than the contributions derived from experiment.

The second half of the table shows the long-range (polarization model) calculations, including the H_1+H_4 corrections to the polarizabilities from Table I and the full dipole retardation contribution as calculated by Babb and Spruch [16] and also by Au [17]. The higher-order H_2 corrections (to order $\alpha^2\langle r_2^{-6}\rangle$) calculated above are also included. Finally, the asymptotic form of the one-electron Lamb shifts as calculated by Goldman and Drake [21] are included. These are due to the effect of the Rydberg electron on the core electron's Lamb shift,

TABLE II. The corrections to the polarizabilities due to H_2. The contributions are given for $n=10$, $L=3$–9. The second column gives the H_2 contributions calculated by Drake [12]. The third column gives the leading $\langle r_2^{-4}\rangle$ contribution, with the next column giving the higher-order $\langle r_2^{-5}\rangle$ and $\langle r_2^{-6}\rangle$ contributions. The fifth column gives the total of the previous two columns, and is thus the total contribution in the polarization potential calculations. The final column gives the difference between the polarization potential results and the variational calculations. All values are in MHz.

	Variational[a]	$\alpha^2\langle r_2^{-4}\rangle/4$	$\frac{3}{16}\langle r^{-5}\rangle-\frac{3}{8}\langle r^{-6}\rangle$ $-\frac{3}{64}l(l+1)\langle r^{-6}\rangle$	Total	Difference
10F	0.2696	0.2670	−0.0010	0.2660	0.0036
10G	0.072 183	0.070 783	0.001 315	0.072 098	0.000 085
10H	0.024 919	0.024 502	0.000 416	0.024 918	0.000 001
10I	0.010 169	0.010 034	0.000 136	0.010 170	−0.000 001
10K	0.004 653	0.004 605	0.000 048	0.004 653	0.000 000
10L		0.002 290	0.000 019	0.002 309	
10M		0.001 205	0.000 008	0.001 213	

[a]Reference [12], Table 9, with the mass correction due to the scaling of the Rydberg subtracted out.

TABLE III. Comparison between theory and experiment for $n=10$ intervals. The energy intervals listed are the separations between the statistically weighted mean of the energies of the four $10L$ spin structure levels and the statistically weighted mean of the $10L+1$ energies. Comparisons are made for both variational calculations of Drake and the polarization potential calculations. All values are in MHz, with one-standard-deviation-error estimates in parentheses.

	$10F$-G	$10G$-H	$10H$-I	$10I$-K	$10K$-L
E_{nr} [a]	2025.9805	484.060 44	152.194 64	57.238 79	24.4346(2)
Expt.[b]	2036.5588(22)	491.005 23(49)	157.052 41(23)	60.815 95(20)	27.1747(5)
Expt.-E_{nr}	10.5783(22)	6.944 79(49)	4.857 77(23)	3.577 16(20)	2.7401(5)
		Drake[a] variational relativistic and radiative effects			
ΔE_{rel}	10.5268(3)	6.930 06(10)	4.852 78(5)	3.575 32(1)	
$L1$	+0.0549(1)	+0.012 91	+0.003 97	+0.001 46	
$L2$	+0.0123	+0.004 84	+0.002 28	+0.001 22	
V''_{ret} [c]	−0.0012	−0.000 71	−0.000 45	−0.000 30	
Total	10.5928(3)	6.947 10(10)	4.858 58(5)	3.577 70(1)	
E-T	−0.0145(22)	−0.002 31(50)	−0.000 81(24)	−0.000 54(20)	
	Long-range interaction predictions for relativistic and radiative corrections				
p^4 [d]	11.1216	7.077 35	4.899 71	3.593 11	2.7477
H_1+H_4 corr. to pol. pot'l[e]	−0.3780	−0.099 52	−0.032 19	−0.012 28	−0.0053
V_{ret} dipole[f]	−0.1853	−0.042 20	−0.012 64	−0.004 52	−0.0018
$\alpha^2\langle r_2^{-6}\rangle H_2$ corr.[g]	+0.0024	−0.000 90	−0.000 28	−0.000 09	−0.0000
Lamb shift	+0.0532	+0.012 90	+0.003 98	+0.001 46	+0.0006
Total	10.6139	6.947 63	4.858 58	3.577 68	2.7412
$E-T$	−0.0356(22)	−0.002 84(49)	−0.000 81(23)	−0.000 52(20)	−0.0011(5)

[a] Reference [4] (and Ref. [3] for the $10K$-$10L$ nonrelativistic energy).
[b] References [5] and [6].
[c] Reference [17].
[d] Reference [13].
[e] Table I.
[f] Reference [16].
[g] Column 4 of Table II.

as well as the Lamb shift of the Rydberg electron. The largest of the terms given by Goldman and Drake are (approximately)

$$-26\,193\ \mathrm{MHz}\langle r_2^{-4}\rangle_{nl}+38\,082\ \mathrm{MHz}\langle r_2^{-6}\rangle_{nl} - 1085\ \mathrm{MHz}\beta_{nl}/n^3\ , \quad (55)$$

where β_{nl} is the hydrogenic Bethe logarithm [22].

The total relativistic and radiative corrections in the long-range model are in fair agreement with the variational calculations, with the agreement becoming very good at high L ($10H$-I and $10I$-K). The agreement between experiment and the long-range calculations is very poor, being somewhat worse than the agreement between the variational calculations and experiment for the low-L intervals. The relatively good agreement observed previously [5] for long-range calculations appears to have been fortuitous, since the agreement worsens when the higher-order relativistic corrections calculated in the present work are included. The remaining discrepancy between experiment and both calculations seems to indicate the presence of additional effects not included in either calculation.

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APPENDIX: HELIUMLIKE IONS

Although the principal reason for the present calculations is to compare with precisely measured helium intervals, it should be noted that the calculations presented can also be used to calculate the energy levels of heliumlike ions. The Z dependence of the various terms can be obtained from the perturbation-theory expressions by noting that matrix elements of H_{1C} and H_4 scale as Z^4, H_{1R} as $(Z-1)^4$, $H_2^{(k)}$ as $(Z-1)^{k+1}/Z^{k-2}$, $V_c^{(k)}$ as $(Z-1)^{k+1}/Z^k$, and Rydberg and core energy differences scale as $(Z-1)^2$ and Z^2, respectively. Using this method, one finds that the overall scaling of the relativistic corrections to β_1 [Eq. (31)] is $(Z-1)^6/Z^4$. Note that the $(Z-1)^6$ scaling is already contained in $\langle r_2^{-6}\rangle$, so that the result for heliumlike ions is $-2063\alpha^2\langle r_2^{-6}\rangle/96Z^4$. It thus has similar scaling as the previously calculated relativistic correction to α_2 [3]. The overall scaling of the H_{1R} corrections of Eqs. (33) and (34) is $(Z-1)^8/Z^6$, which differs from the scaling of the larger H_{1R} correction of Eq. (32), which scales as $(Z-1)^6/Z^4$ [12]. Finally, the $\alpha^2\langle r_2^{-4}\rangle$ contribution from H_2 [Eq. (54)] scales as $(Z-1)^4/Z^2$, while the $\alpha^2\langle r_2^{-6}\rangle$ contribution has an overall scaling of $(Z-1)^6/Z^4$. The scaling of other previously calculated terms is discussed elsewhere [1,3,12].

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