Variational Eigenvalues for the Rydberg States of Helium: Comparison with Experiment and with Asymptotic Expansions

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High-precision variational eigenvalues are presented for a range of helium Rydberg states up to $n=10$ and $L=7$. Convergence to a few parts in 10^{18} is obtained for many of the nonrelativistic eigenvalues. The results allow a clear assessment of the accuracy of asymptotic expansion methods extensively developed for states of high angular momentum. After adding relativistic and radiative corrections, a comparison with new high-precision measurements for transitions among the $n=10$ states is made. Contributions from the long-range Casimir-Polder effect are discussed.

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The energy splittings among the $n=10$ state of helium have recently been the subject of intense study, both theoretically and experimentally. On the experimental side, improvements in accuracy to better than ± 1 kHz for the measured splittings[1] make the measurements sensitive to small radiative and retardation effects of the Casimir-Polder type.[2,3] The latter, which have never been clearly verified experimentally, provide a primary motivation for the high-precision measurements. However, all the ordinary (nonretarded) contributions must first be known to sufficient precision so that they can be subtracted from the measured intervals.

On the theoretical side, the $n=10$ states lie in the intermediate range of excitation dividing low-lying states, where established variational methods for the entire two-electron wave function are applicable, and high-lying states where asymptotic expansion methods based on a core-polarization model become extremely accurate.[4] In the latter model, exchange effects are neglected, and the outer electron is regarded as moving in the field of a polarizable core consisting of the nucleus and a tightly bound inner electron. As the degree of excitation increases, traditional variational methods deteriorate rapidly in accuracy while the core-polarization model becomes progressively more accurate, especially with increasing angular momentum L. Recent advances in variational technique[5,6] now make it possible to extend high-precision variational calculations into the intermediate nL range, thereby allowing an assessment of the accuracy of the truncated asymptotic expansions generated by the core-polarization model.

The purpose of this Letter is to report the results of variational calculations for a range of states up to $n=10$ and $L=7$ with the dual purpose of comparing with the new measurements, and with the core-polarization model. The nonrelativistic eigenvalues obtained in this work are the most accurate variational bounds in the literature for any few-body system.

The method of calculation has been described previously,[5,6] and is only briefly summarized here. The method is an extension of the older Hylleraas-type variational calculations. Here, the two-electron wave function is expanded in the finite basis set

$$\Psi(\mathbf{r}_1,\mathbf{r}_2)=\sum_{l_1,l_2}\sum_{p}\sum_{i,j,k} a_{ijk}^{(t)} r_1^i r_2^j r_{12}^k \exp[-\alpha^{(t)}r_1-\beta^{(t)}r_2](l_1l_2;L)\pm\text{exchange}\,, \qquad (1)$$

where $r_{12}=|\mathbf{r}_1-\mathbf{r}_2|$ is the interelectronic coordinate, $(l_1l_2;L)$ denotes a vector-coupled product of spherical harmonics to form a state of total angular momentum L, t denotes the collection of labels (l_1,l_2,p), the $a_{ijk}^{(t)}$ are linear variational coefficients, and the sum over i,j,k is such that $i+j+k\le N$, with N an integer which is progressively increased to systematically enlarge the basis set. The sum over l_1,l_2 covers the values

$$(l_1,l_2)=(0,L),\ (1,L-1),\ \ldots,\ ([L/2],L-[L/2])\,, \qquad (2)$$

as required for completeness. The novel features in the present work include the sum over p, which allows each combination of powers i,j,k to appear more than once with different exponential scale factors $\alpha^{(t)}$ and $\beta^{(t)}$, thereby producing a "doubled" basis set. This is crucial for excited states because at least two distance scales in fact need to be represented for each electron. In addition, the screened hydrogenic wave function $\Phi_{1s}(\mathbf{r}_1,Z)\times\Phi_{nL}(\mathbf{r}_2,Z-1)$ is included explicitly in the basis set with an independent linear variational coefficient, and a complete optimization is performed with respect to the $\alpha^{(t)},\beta^{(t)}$. The results with up to 750 terms show good numerical stability when performed with 80-bit (extended precision) arithmetic on a Definicon DSI/780 board. The longest calculation takes less than an hour of microcomputer time. All the final results were checked with 120-bit (quadruple precision) arithmetic.

For high-L states where exchange effects are negligible, the main source of uncertainty in the core-polarization model is the nonrelativistic energy, rather than the smaller relativistic and radiative corrections. Table I shows the nonrelativistic variational eigenvalues for infinite nuclear mass obtained in this work, expressed as a correction ΔE to the screened hydrogenic energy

$$E_{\rm SH} = -2 - 1/2n^2 \text{ a.u.} \tag{3}$$

Except for the $10G$ and $10H$ results published previously,[6] these are the first variational calculations for $L > 3$. The final results were extrapolated below the variational upper bounds by studying the convergence with increasing N up to about 700 terms. The numbers in parentheses in Table I indicate the total amount of extrapolation in the final figure quoted, and can be taken as a conservative estimate of the uncertainty. Many of the eigenvalues have converged to better than $\pm 10^{-18}$ a.u. The singlet-triplet splittings remain clearly resolved for all states up to $10I$, but are no longer visible to this degree of precision for the K states. Full details of the calculations will be presented in a future publication.

Table II compares the singlet-triplet average of the energies in Table I with the asymptotic expansion method of Drachman,[4] computed according to his prescription

$$\Delta E = V_4 + V_6 + \tfrac{1}{2}(V_7+V_8) + \Delta_2 \pm \tfrac{1}{2}(V_7+V_8)\,, \tag{4}$$

where V_i is the core multipole contribution proportional to $\langle R^{-i}\rangle$ and Δ_2 is the second-order dipole correction. It is clear that the spectacularly good agreement found previously[6] for the $10G$ and $10H$ ($L=4$ and 5) states is a fortuitous coincidence caused by a crossing of the two sets of calculations near $n=10$. In general, the differences listed in the last column of Table II are about the same as, or slightly larger than, the estimated error of $\pm\frac{1}{2}(V_7+V_8)$ [see Eq. (4)] due to the truncation of the asymptotic expansion. On the whole, this provides a remarkably good estimate of the error.

Turning now to the comparison with experiment, Table III summarizes the contributions to the energy for the $10I$ and $10K$ states. The entries in the table are as follows. $\Delta E_{\rm nr}$ is the correction to the screened hydrogenic energy $E_{\rm SH}$, $\Delta E_M^{(1)}$ and $\Delta E_M^{(2)}$ are the first- and second-order mass polarization corrections, $\Delta E_{\rm rel}$ is the relativistic correction, $\Delta E_{\rm anom}$ is the anomalous magnetic moment correction, $\Delta E_{\rm st}$ is the singlet-triplet mixing correction, $(\Delta E_{\rm RR})_M$ is the relativistic reduced-mass correction from the mass scaling of the Breit interaction together with the Stone[7] terms, $(\Delta E_{\rm RR})_X$ is a second-order cross term between the Breit interaction and the mass polarization operator, and $\Delta E_{L,1}$ and $\Delta E_{L,2}$ are one- and two-electron Lamb-shift corrections. Detailed expressions for all of these terms have been given previously,[5] and will not be repeated here. All are expressed relative to the $\mathrm{He}^+(1s)$ state. Combining these with the $10G$ and $10H$ results published previously[6] yields the comparison with experiment shown in Table IV.

Before discussing the results, a word of clarification is necessary concerning retardation effects. The main part of what Au and co-workers[3,8] refer to as retardation is

TABLE I. Variational eigenvalues for the Rydberg states of helium, expressed as a correction $\Delta E_{\rm nr}$ to the screened hydrogenic energy $E_{\rm SH}$ [see Eq. (3)]. Units are 10^{-7} a.u.

L	n	$\Delta E_{\rm nr}$(singlet)	$\Delta E_{\rm nr}$(triplet)
4	5	−7.10898584711(4)	−7.10925343922(2)
4	6	−4.5649842434(3)	−4.5652806407(3)
4	7	−3.0459211947(5)	−3.0461756486(5)
4	8	−2.1149402399(1)	−2.1151442474(1)
4	9	−1.5212141342(7)	−1.521374920(1)
4	10	−1.1276431780(2)	−1.1277700278(4)
5	6	−1.458653908316(4)	−1.45865412665(1)
5	7	−1.01173828962(2)	−1.01173858977(1)
5	8	−0.7182865580(1)	−0.7182868573(1)
5	9	−0.523974464(1)	−0.523974732(1)
5	10	−0.3921439451(1)	−0.3921441740(1)
6	7	−0.389735382601(1)	−0.389735382737(1)
6	8	−0.285495845850(2)	−0.285495846075(4)
6	9	−0.212262097328(9)	−0.212262097577(6)
6	10	−0.160865161922(2)	−0.160865162169(2)
7	8	−0.125702293050(0)	−0 125702293050(0)
7	9	−0.095901569403(0)	−0.095901569403(0)
7	10	−0.073883758766(2)	−0.073883758767(4)

TABLE II. Comparison of the spin-averaged variational eigenvalues $\Delta\bar{E}_{\rm var}$ from Table I with the values $\Delta\bar{E}_{\rm pol}$ from the core-polarization model (in MHz).

L	n	$\Delta\bar{E}_{\rm var}$	$\Delta\bar{E}_{\rm pol}$	difference
4	5	−4676.93484501(2)	−4677.0794±1.01	0.144
4	6	−3003.3011205(2)	−3003.3636±1.19	0.063
4	7	−2003.9288573(4)	−2003.9559±1.04	0.027
4	8	−1391.4401873(1)	−1391.4521±0.84	0.0118
4	9	−1000.826507(1)	−1000.8316±0.66	0.0051
4	10	−741.8935917(2)	−741.8955±0.52	0.0020
5	6	−959.61668162(1)	−959.6281±0.0022	0.0144
5	7	−665.60066508(1)	−665.6052±0.0074	0.0045
5	8	−472.5451674(1)	−472.5461±0.0105	0.0009
5	9	−344.711466(1)	−344.7108±0.0106	−0.0007
5	10	−257.9830286(1)	−257.9817±0.0097	−0.0013
6	7	−256.3984126065(4)	−256.40021±0.00161	0.00180
6	8	−187.821493674(2)	−187.82280±0.00103	0.00131
6	9	−139 64260691(1)	−139.64349±0.00059	0.00088
6	10	−105.829683489(1)	−105.83027±0.00032	0.00059
7	8	−82.6967984749(0)	−82.69709±0.00028	0.00029
7	9	−63.0915519990(2)	−63.09180±0.00023	0.00025
7	10	−48.606514337(2)	−48.60671±0.00018	0.00019
8	9		−30.71236±0.00005	
8	10		−24.17868±0.00005	

TABLE III. Contributions to the $10I$ and $10K$ state energies of ^{4}He relative to $He^+(1s)$ (in MHz). $Ry_\infty = 109\,737.315\,709$ cm^{-1}, $Ry_M = 109\,722.273\,515$ cm^{-1}, $\alpha^{-1} = 137.0358985$, and $\mu/M = 0.000\,137\,074\,5620$.

Term	$10\,^1I_6$	$10\,^3I_5$	$10\,^3I_6$	$10\,^3I_7$	$10\,^1K_7$	$10\,^3K_6$	$10\,^3K_7$	$10\,^3K_8$
ΔE_{nr}	-105.82968	-105.82968	-105.82968	-105.82968	-48.60651	-48.60651	-48.60651	-48.60651
$\Delta E_M^{(1)}$	-0.02891	-0.02891	-0.02891	-0.02891	-0.01330	-0.01330	-0.01330	-0.01330
$\Delta E_M^{(2)}$	-0.61807	-0.61807	-0.61807	-0.61807	-0.61806	-0.61806	-0.61806	-0.61806
ΔE_{rel}	-13.77802	-11.12404	-14.09883	-15.44622	-10.20270	-8.27782	-10.41123	-11.49067
ΔE_{anom}	0.00000	0.00094	-0.00149	0.00060	0.00000	0.00059	-0.00097	0.00040
ΔE_{st}	6.08749	0.00000	-6.08749	0.00000	4.58476	0.00000	-4.58476	0.00000
$(\Delta E_{RR})_M$	-0.00687	-0.00822	-0.00687	-0.00589	-0.00540	-0.00639	-0.00540	-0.00465
$(\Delta E_{RR})_X$	0.00621	0.00683	0.00630	0.00568	0.00474	0.00520	0.00480	0.00434
$\Delta E_{L,1}$	-0.00261	-0.00261	-0.00261	-0.00261	-0.00116	-0.00116	-0.00116	-0.00116
$\Delta E_{L,2}$	-0.00348	-0.00348	-0.00348	-0.00348	-0.00226	-0.00226	-0.00226	-0.00226
Total	-114.17394	-117.60724	-126.67114	-121.92858	-54.85990	-57.51972	-64.23887	-60.73188

included automatically in the present calculations through the H_2 orbit-orbit interaction term in the Breit interaction, and the $\Delta E_{L,2}$ two-electron QED correction. These two terms correspond to the leading two terms in the expansion of the retardation potential due to two-photon exchange[2,3,8] (in atomic units),

$$\Delta V_{ret} = \frac{\alpha^2}{4}\left(\frac{a_0}{R}\right)^4 - \frac{7\alpha^3}{6\pi}\left(\frac{a_0}{R}\right)^3 + O(\alpha^4(a_0/R)^2). \quad (5)$$

TABLE IV. Comparison of theory and experiment for the $10G$-$10H$, $10H$-$10I$, and $10I$-$10K$ transition frequencies of ^{4}He (in MHz). The weighted mean transition frequencies are calculated from Eq. (6) of Ref. 10.

Transition	Experiment[a]	Theory	Difference
$^1G_4 - {}^1H_5$	486.8622(7)	486.8612	0.0010(7)
$^3G_3 - {}^3H_4$	488.6677(9)	488.6663	0.0014(9)
$^3G_4 - {}^3H_5$	495.5571(6)	495.5578	-0 0007(7)
$^3G_5 - {}^3H_6$	491.9668(7)	491.9662	0.0006(6)
$(G-H)_{mean}$	491.0087(5)	491.0082	0.0005(5)
$^1H_5 - {}^1I_6$	154.6689(4)	154.6686	0.0003(4)
$^3H_4 - {}^3I_5$	155.8155(5)	155.8150	0.0005(5)
$^3H_5 - {}^3I_6$	159.6490(5)	159.6496	-0.0006(5)
$^3H_6 - {}^3I_7$	157.6299(4)	157.6305	-0.0006(4)
$(H-I)_{mean}$	157.0535(2)	157.0537	-0.0002(2)
$^1I_6 - {}^1K_7$	59.3131(4)	59.3140	-0.0009(4)
$^3I_5 - {}^3K_6$	60.0876(5)	60.0875	0.0001(5)
$^3I_6 - {}^3K_7$	62.4320(4)	62.4323	-0.0003(4)
$^3I_7 - {}^3K_8$	61.1966(3)	61 1967	-0.0001(3)
$(I-K)_{mean}$	60.8165(2)	60.8168	-0 0003(2)

[a]Reference 1.

What is missing is the small (< 1 kHz) Casimir-Polder long-range deviation of H_2 and $\Delta E_{L,2}$ from the short-range forms used here. Taking the difference between the fully retarded values[2,3,8] and the results of Eq. (5) gives additional contributions of -0.720, -0.454, and -0.305 kHz, respectively, to the G-H, H-I, and I-K transition frequencies. It is only at this level that retardation effects are not included in the present calculation, and might appear as a discrepancy between the calculations and experiment. This is the part which reflects the incipient change in the power-law dependence of the long-range potential predicted by the Casimir-Polder effect.

The results in Table IV show that discrepancies of 1.0 ± 0.7 and 1.4 ± 0.9 kHz are present for two of the four G-H magnetic structure transitions. This is too large and in the wrong direction to be explained by the above residual retardation effects. However, for this transition, there is a fairly large one-electron QED correction (denoted by $\Delta E_{L,1}$ in Table III) of -12.8 kHz coming primarily from the core-electron Lamb shift. It may be that the simple screening approximation used to calculate it[6,9] is not adequate. The effect of the correction is to produce a common shift to all four magnetic structure components. For the H-I and I-K transitions, the corresponding QED corrections reduce to -3.96 and -1.45 kHz, respectively. For these transitions, the discrepancies for the weighted mean of the four magnetic structure components[10] are -0.2 ± 0.2 and -0.3 ± 0.2 kHz in the two cases.[1] This is nearly within experimental error, but including the above retardation corrections changes the discrepancies to 0.25 ± 0.2 and 0.0 ± 0.2 kHz, respectively. This is clearly an improvement for the I-K transition for which the theoretical QED correction should be the most reliable. To this marginal extent, the experimental results show evidence for the change in the power-law dependence predicted by the Casimir-Polder effect.[2,3,8] The total retardation potential due to two-photon exchange is verified to better than 10% as stated in Ref. 1.

In conclusion, this paper presents high-precision variational calculations for a range of Rydberg states up to $n=10$ and $L=7$. The results clearly establish the validity of accuracy estimates for asymptotic expansions based on a core-polarization model. Combining the latter with variational results up to $n=10$ covers nearly all states of helium (and by extension, two-electron ions). It is only the high-n, low-L states which remains an open problem. Comparison with experiment verifies the total long-range retardation potential to better than 10% and shows marginal evidence for the change in the power-law dependence predicted by the Casimir-Polder effect. The weakest part of the calculation, which still requires further work, is the evaluation of radiative corrections for Rydberg states. A full account of this work will be presented in a forthcoming publication.

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