PHYSICAL REVIEW A VOLUME 47, NUMBER 1 JANUARY 1993

Rydberg states of helium: Some further small corrections

Richard J. Drachman
Laboratory for Astronomy and Solar Physics, NASA Goddard Space Flight Center, Greenbelt, Maryland 20771

(Received 6 July 1992)

The optical-potential method based on the Feshbach projection-operator formalism has been successfully applied to the computation of fine-structure splittings between highly excited levels of helium [R. J. Drachman, Phys. Rev. A **26**, 1228 (1982)]. In this paper, I report additional terms in the nonrelativistic effective potential decreasing as x^{-9} and x^{-10}, where x is the distance of the outer electron from the He^{+} core. They involve higher-multipole distortions of the wave function of the core electron, higher nonadiabatic corrections, and perturbation theory up to fourth order in the electrostatic potential. Energy shifts due to these terms are compared with the extremely accurate variational results of Drake [Phys. Rev. Lett. **65**, 2769 (1990)].

PACS number(s): 31.20.−d, 31.50.+w

In a series of papers [1–4] the calculation of energy levels of the helium atom in nonpenetrating (high-L) states has been put on a fairly systematic basis, based on a long history [5]. The method makes use of several expansions: perturbation theory, multipole series, and a very important expansion in "nonadiabatic" order. The convergence improves very rapidly with increasing angular momentum L and is quite consistent with the best variational calculations [6] for sufficiently high L. Although the expansions appear only to be asymptotic and hence have an unavoidable, irreducible error, the fact that the result is in the form of an analytic expansion makes it quite useful, and it is the aim of the present paper to summarize previous results and to present some further and shorter-range corrections.

We use an optical-potential method, as described in Ref. [1], hereafter referred to as I, to calculate deviations of the Rydberg energy levels from their unperturbed hydrogenic values. That is, the unperturbed Hamiltonian of the two-electron system is taken to be

$$H_0=-\nabla_r^2-\frac{4}{r}-\mu\left[\nabla_x^2+\frac{2}{x}\right] , \tag{1}$$

where energies are in reduced Rydberg units $\mathcal{R}$. The coordinate r is the position of the inner (core) electron relative to the nucleus, and x is the position of the outer (Rydberg) electron relative to the center of mass of the one-electron core, each measured in an appropriately scaled distance unit. (These convenient Jacobi coordinates were introduced in Ref. [4]; their use eliminates the usual mass-polarization term involving the operator $\nabla_1\cdot\nabla_2$ and localizes the effect of nuclear recoil in the perturbing potential.) The appropriate definitions are as follows [4]:

$$\mathbf{r}=m(\mathbf{r}_1-\mathbf{r}_M) , \quad \mathbf{x}=m'\left[\mathbf{r}_2-m\mathbf{r}_M-\frac{K}{2}\mathbf{r}_1\right] , \tag{2}$$

where $K=2/(1+M)$, $m=1-K/2$, $m'=1/(1+K/2)$, and $\mu=m'/m=1/(1-K^2/4)$. Here r_1, r_2, and r_M are the coordinates of the core electron, the Rydberg electron, and the nucleus, respectively, measured in the laboratory frame. The parameter K measures the nuclear recoil and equals 2.7415×10^{-4} for the case of $^4\mathrm{He}$, the electron mass is taken as unity, and the nuclear mass is M. The reduced Rydberg unit of energy is $\mathcal{R}=m\,\mathrm{Ry}=3.289\,390\,995\times10^{9}$ MHz.

In these coordinates the perturbing potential has the form

$$V(\mathbf{x},\mathbf{r})=\mu\left[\frac{2}{x}+\frac{2}{|\mathbf{x}-m'\mathbf{r}|}-\frac{4}{|\mathbf{x}+(K\mu/2)\mathbf{r}|}\right] . \tag{3}$$

We will be interested in cases where $x\gg r$, so V can be expanded as

$$V(\mathbf{x},\mathbf{r})=\sum_{q=1}^{\infty}C_q\frac{2r^q}{x^{q+1}}p_q(x\cdot r) ,$$

$$C_q=\mu[m'^q-2(-K\mu/2)^q] . \tag{4}$$

(These equations are patterned after those in I, the main difference being the use here of Jacobi coordinates. In I the coefficient $C_q=1$, and the mass-polarization term appears instead.)

As before [1], the optical potential U_0 gives most of the contribution to the shift in the Rydberg levels; the first-order shift is

$$\Delta_1=\int d^3x\ \Psi_0(\mathbf{x})\ U_0\Psi_0(\mathbf{x}) , \tag{5}$$

where $\Psi_0(x)$ is the unperturbed Rydberg state. As in I the lowest order optical potential has the following form:

$$U_0=\sum_{j_1}\langle 1s|V|n\rangle\frac{h^{j_1-1}}{(d_n)^{j_1}}\langle n|V|1s\rangle+\sum_{j_1,j_2}\frac{\langle 1s|V|n\rangle h^{j_1-1}\langle n|V|m\rangle h^{j_2-1}\langle m|V|1s\rangle}{(d_n)^{j_1}(d_m)^{j_2}}$$
$$+\sum_{j_1,j_2,j_3}\frac{\langle 1s|V|n\rangle h^{j_1-1}\langle n|V|m\rangle h^{j_2-1}\langle m|V|p\rangle h^{j_3-1}\langle p|V|1s\rangle}{(d_n)^{j_1}(d_m)^{j_2}(d_p)^{j_3}}+\cdots , \tag{6}$$

where $h=\mu[-\nabla_x^2-(2/x)+(1/N^2)]$ and $d_n=E_{1s}-E_n=4(1/n^2-1)$.

This has the form of an ordinary perturbation series, except for the nonadiabatic factors involving h/d_n, each additional power of which produces an additional factor of x^{-2}. (As in I, lower case indices refer to states of the core, and upper case to states of the outer electron.) All repeated indices (n,m,p) are summed over a complete set of states excluding 1s, and the nonadiabatic indices (j_1,j_2,j_3) begin with 1 and are summed until the desired maximum negative power of x (here x^{-10}) is reached.

To specify a particular type of term in U_0 we will use the following definitions. Let k be the perturbation order of the term, the number of factors of V appearing in it. Then define the nonadiabatic order of the term by the parameter J, where

$$J=\sum_{i=1}^{k-1}(j_i)-k+1\ . \tag{7}$$

Then we can label a particular type of term in the optical potential as $U_0[J]$ to indicate the nonadiabatic order ($J=0$–3). All the adiabatic terms ($J=0$) in Eq. (6) can be evaluated in a straightforward way using the method of Dalgarno and Lewis [7] to evaluate the sums over intermediate states, as discussed in I. In addition, Au [8] has given a general (although complicated) expression for such terms; this part of the problem can be considered to be completely solved. It is also easy to evaluate sums whose denominators contain d_n to powers $j_i\neq1$ either using repeated application of the method of Ref. [7] or with the formulas of Ref. [8]. The remaining difficulty involves the effect of the operator h whenever $J\neq0$, and that involves some intricate algebra.

Up to x^{-10} the $J=0$ part of the potential is

$$U_0[0]=-\frac{9(1+K)}{32x^4}-\frac{15(1-2K)}{64x^6}-\frac{525}{1024x^8}-\frac{8505}{4096x^{10}}+\frac{213}{512x^7}+\frac{1773}{1024x^9}-\frac{4329}{32\,768x^8}-\frac{137\,751}{65\,536x^{10}}\ . \tag{8}$$

Here the first four terms are of second order in V, the next two are of third order, and the seventh and eighth are of fourth order. We have retained the finite-mass corrections of order K only in the two leading terms; beyond that point they are certainly negligible.

The total $J=1$ (nonadiabatic) part of the potential up to x^{-10} is

$$U_0[1]=\frac{129(1+K)}{256x^6}+\frac{1605}{2048x^8}+\frac{22\,855}{8192x^{10}}-\frac{28\,491}{8192x^9}+\frac{791\,313}{524\,288x^{10}}\ . \tag{9}$$

Here the first three terms are of second order, the fourth of third order, and the last of fourth order in V.

Next we calculate the "second nonadiabatic" terms, those with $J=2$. Up to x^{-10} these are no higher than second order in V and include dipole and quadrupole terms in the multipole expansion. Here the operator h appears twice; it is convenient to commute one to the right and the other to the left. The resulting expression is complicated and energy dependent, but as before we prefer to eliminate the energy dependence in favor of some terms of higher order in $1/x$. The result up to x^{-10} is

$$U_0[2]=\frac{319}{3840x^7}-\frac{957}{512x^8}\left[1+\frac{L(L+1)}{10}\right]+\frac{7197}{114\,688x^9}-\frac{35\,985}{8192x^{10}}\left[1+\frac{L(L+1)}{21}\right]\ . \tag{10}$$

The first two terms (reported previously) are from the dipole term in the potential, and the last two are from the quadrupole.

Next we display the $J=3$ term, which is of second order in V and includes only dipole parts. The result is

$$U_0[3]=-\frac{493\,323}{516\,096x^9}+\frac{48\,365}{4096x^{10}}\left[1+\frac{3L(L+1)}{14}\right]\ . \tag{11}$$

TABLE I. Second-order energy shifts, D_2, in MHz for helium with $K=0$. (Numbers in brackets are multiplicative powers of 10.) The first entry in each case is due to the adiabatic dipole alone, $D_2(4,4)$, and the second is due to the cross term between $1/x^4$ and $1/x^6$ terms, $D_2(4,6)$.

$N \backslash L$	3	4	5	6	7	8	9
5	−26.265 20 5.583 69	−0.956 18 0.023 14					
6	−17.143 33 3.976 68	−0.721 23 0.022 20	−0.052 880 4.024[−4]				
7	−11.510 55 2.803 33	−0.517 15 0.017 73	−0.042 838 4.208[−4]	−4.8680[−3] 1.56[−5]			
8	−8.010 65 2.011 98	−0.373 14 0.013 62	−0.032 816 3.639[−4]	−4.1369[−3] 1.73[−5]	−6.382[−4] 1.02[−6]		
9	−5.764 78 1.478 69	−0.274 52 0.010 43	−0.024 992 2.976[−4]	−3.3257[−3] 1.54[−5][b]	−5.609[−4] 1.17[−6]	−1.086[−4] 9.7[−8]	
10	−4.271 95 1.112 52	−0.206 40 8.06[−3][a]	−0.019 208 2.398[−4]	−2.6404[−3] 1.36[−5]	−4.676[−4] 1.12[−6]	−9.781[−5] 1.1[−7]	−2.259[−5] 1.3[−8]

[a] Value supplied by G. W. F. Drake.

[b] Value may be low by about 2%.

TABLE II. Total nonrelativistic energy shifts in MHz for helium with $K=0$. The various terms Δ_p are the expectation values of the terms of Eq. (15), and the asymptotic series is terminated by including one-half of the smallest term as described in the text. The numbers in brackets are multiplicative powers of 10.

N	L	Δ_4	Δ_6	$\Delta_7+\Delta_8$	$\Delta_9+\Delta_{10}$	D_2	Total nonrel.
5	4	−4699.1300	24.0178	−2.0219	4.4870	−0.9330	−4677.0562±1.011
6		−3021.5599	20.1088	−2.3824	4.9756	−0.6992	−3003.3415±1.191
7		−2017.5222	15.1205	−2.0742	4.2755	−0.4994	−2003.9382±1.037
8		−1401.4684	11.2248	−1.6707	3.4303	−0.3595	−1391.4385±0.835
9		−1008.317 04	8.419 50	−1.319 05	2.704 95	−0.264 09	−1000.8212±0.660
10		−747.588 86	6.420 40	−1.041 34	2.134 82	−0.198 34	−741.8875±0.521
6	5	−961.405 432	1.828 069	0.004 327	0.012 388	−0.052 478	−959.6277±0.0022
7		−667.212 052	1.657 043	−0.014 705	0.016 305	−0.042 417	−665.6048±0.0074
8		−473.841 725	1.338 969	−0.020 995	0.015 826	−0.032 452	−472.5483±0.0079
9		−345.728 576	1.053 466	−0.021 297	0.013 899	−0.024 694	−344.7142±0.0069
10		−258.780 760	0.827 973	−0.019 384	0.011 748	−0.018 968	−257.9853±0.0059
7	6	−256.620 0199	0.223 0635	0.003 2219	0.000 1926	−0.004 8524	−256.398 49±0.000 10
8		−188.032 4304	0.212 7334	0.002 0645	0.000 2873	−0.004 1196	−187.821 61±0.000 14
9		−139.821 8183	0.181 0644	0.001 1829	0.000 3061	−0.003 3103	−139.642 73±0.000 15
10		−105.976 8829	0.148 9302	0.000 6384	0.000 2889	−0.002 6268	−105.829 80±0.000 14
8	7	−82.734 2694	0.037 5412	0.000 5604	6.85[−6]	−0.000 6372	−82.696 8016±3×10^{-6}
9		−63.128 5075	0.037 0359	0.000 4685	1.127[−5]	−0.000 5597	−63.091 5572±6×10^{-6}
10		−48.639 1850	0.032 7654	0.000 3593	1.292[−5]	−0.000 4665	−48.606 5203±6×10^{-6}
9	8	−30.720 289 75	0.007 988 14	0.000 105 78	4.11[−7]	−0.000 108 50	−30.712 304 12±2×10^{-7}
10		−24.186 698 53	0.008 065 92	0.000 097 30	7.33[−7]	−0.000 097 70	−24.178 632 64±4×10^{-7}

TABLE III. Comparison of the asymptotic nonrelativistic energy shifts in MHz with the accurate variational results of Ref. [6] for helium with $K=0$. Note that the estimated error is in substantial agreement with the actual deviation in most cases; the very close agreement for $L=4$ is accidential.

N	L	Asymptotic	Variational	$V-A$
5	4	−4677.0562±1.011	−4676.934 845 01	0.1213
6		−3003.3415±1.191	−3003.301 1205	0.0404
7		−2003.9382±1.037	−2003.928 8573	0.0093
8		−1391.4385±0.835	−1391.440 1873	−0.0017
9		−1000.8212±0.660	−1000.826 507	−0.0053
10		−741.8875±0.521	−741.893 5917	−0.0061
6	5	−959.6277±0.0022	−959.616 681 62	0.0110
7		−665.6048±0.0074	−665.600 665 08	0.0041
8		−472.5483±0.0079	−472.545 1674	0.0031
9		−344.7142±0.0069	−344.711 466	0.0027
10		−257.9853±0.0059	−257.983 0286	0.0023
7	6	−256.398 49±0.000 10	−256.398 412 6065	0.000 08
8		−187.821 61±0.000 14	−187.821 493 674	0.00012
9		−139.642 73±0.000 15	−139.642 606 91	0.000 12
10		−105.829 80±0.000 14	−105.829 683 489	0.000 12
8	7	−82.696 8016±3×10^{-6}	−82.696 798 4749	3.1×10^{-6}
9		−63.091 5572±6×10^{-6}	−63.091 551 9990	5.2×10^{-6}
10		−48.606 5203±6×10^{-6}	−48.606 514 337	6.0×10^{-6}
9	8	−30.712 304 12±2×10^{-7}	a	
10		−24.178 632 64±4×10^{-7}	a	

[a] Value not available.

There are two more types of terms to be considered. The first of these is the following addition to the effective potential:

$$U'=\frac{387}{16\,384x^8}+\frac{2253}{65\,536x^{10}}-\frac{24\,427}{131\,072x^{10}}\ . \tag{12}$$

The first two terms here are usually considered to be fourth-order contributions due to the normalization of the wave function, but in our present method they emerge from the second-order shift, Δ_2, as described in Eqs. (43)–(45) of I. The third is a nonadiabatic term of order x^{-10} also coming from Δ_2.

The other is a true second-order perturbation term having the following form:

$$D_2=\sum_{\substack{N,N'\\N'\neq N}}\frac{\langle NL|W|N'L\rangle\langle N'L|W|NL\rangle}{E_N-E_N'}\ ,$$
$$W=-\frac{9}{32x^4}+\frac{69}{256x^6}\ . \tag{13}$$

This expression represents the second-order shift in energy of the outer electron due to the first two terms in the effective potential. The effect of the leading (x^{-4}) term in W has been considered previously in Refs. [1,3], and recently an elegant closed expression has been derived [9]. This correction can be considered (in some sense) to be equivalent to a term of order x^{-8} since it involves two factors of order x^{-4}. It is then necessary to include the cross term between the terms in W of orders x^{-4} and x^{-6} to represent an equivalent x^{-10} correction. Specifically, the cross term has the form

$$D_2(4,6)=-\frac{621}{4096}\sum_{\substack{N,N'\\N'\neq N}}\frac{\langle NL|x^{-4}|N'L\rangle\langle N'L|x^{-6}|NL\rangle}{E_N-E_{N'}}. \tag{14}$$

A table giving the values of $D_2(4,4)$ for a variety of interesting Rydberg states of helium appears in Ref. [3]. Table I gives values of both second-order terms, $D_2(4,4)$ and $D_2(4,6)$, obtained by solving the Dalgarno-Lewis equation based on Eq. (13).

For convenience, we will now display the total nonrelativistic optical potential, up to x^{-10}, summing the terms shown separately above (we have taken $K=0$ here, assuming the nucleus to be infinitely massive, in order to make comparisons with other work):

$$\begin{aligned}U=&-\frac{9}{32x^4}+\frac{69}{256x^6}+\frac{3833}{7680x^7}\\&-\left[\frac{55\,923}{52\,768}+\frac{957}{5120}L(L+1)\right]\frac{1}{x^8}-\frac{908\,185}{344\,064x^9}\\&+\left[\frac{3871\,381}{524\,288}+\frac{33\,275}{14\,336}L(L+1)\right]\frac{1}{x^{10}}+\cdots\ .\end{aligned} \tag{15}$$

In Table II we show results for Rydberg states of helium with $4\leq L\leq 8$ and $5\leq N\leq 10$, displaying the energy shifts corresponding to the expectation values of each term in the effective potential (x^{-k}) as Δk. Since we are dealing with an asymptotic series, we continue to use the criterion for terminating the expansion introduced in I: We include one-half of the smallest term in the sum and estimate the error of the total also to equal one-half of the smallest term. We combine $\Delta_7+\Delta_8$ and $\Delta_9+\Delta_{10}$, since these combinations can be related to each other and should not be treated as independent, as discussed in I. The total second-order energy shift, D_2, is also listed.

Finally, in Table III we compare these results with the excellent variational results of Drake [6]. The agreement is very good, usually well within the estimated errors of the asymptotic expansion, and it improves very rapidly with increasing L. The results presented here continue to support the usefulness of the expansion method. Although it does not match the variational method in accuracy, especially for small values of L, the fact that it is analytic and can be easily applied to any desired state is a significant advantage.

Although this Brief Report has concentrated on helium itself, it is not difficult to scale all the potentials to apply to any two-electron positive ion. A very complete discussion of the whole subject of two-electron Rydberg systems, including relativistic corrections and comparison with the best experiments, is contained in a recent review volume [10].

---

[1] R. J. Drachman, Phys. Rev. A **26**, 1228 (1982).

[2] G. Peach, in *Atoms in Astrophysics,* edited by P. G. Burke *et al.* (Plenum, New York, 1983), pp. 115–71.

[3] R. J. Drachman, Phys. Rev. A **31**, 1253 (1985).

[4] R. J. Drachman, Phys. Rev. A **33**, 2780 (1986); **37**, 979 (1988).

[5] H. A. Bethe, in *Handbuch der Physik* (Edward, Ann Arbor, 1943), Vol. 24, part 1, p. 339; G. Ludwig, Helv. Phys. Acta **7**, 273 (1934); M. H. Mittleman and K. M. Watson, Phys. Rev. **113**, 198 (1959); C. J. Kleinman *et al.*, *ibid.* **165**, 53 (1968); J. Callaway *et al.*, *ibid.* **168**, 12 (1968); R. J. Drachman, *ibid.* **173**, 190 (1968); A. Dalgarno *et al.*, *ibid.* **176**, 194 (1968); C. Deutsch, Phys. Rev. A **2**, 43 (1970); **3**, 1516 (E) (1971); **13**, 2311 (1976); M. J. Seaton and L. Steenman-Clark, J. Phys. B **10**, 2639 (1977); R. J. Drachman, *ibid.* **11**, L699 (1979).

[6] G. W. F. Drake, Phys. Rev. Lett. **65**, 2769 (1990).

[7] A. Dalgarno and J. T. Lewis, Proc. R. Soc. London, Ser. A **233**, 70 (1955).

[8] C. K. Au, Phys. Rev. A **33**, 717 (1986).

[9] G. W. F. Drake and R. A. Swainson, Phys. Rev. A **44**, 5448 (1991).

[10] *Long-Range Casimir Forces: Theory and Recent Experiments in Atomic Systems,* edited by Frank S. Levin and David Micha (Plenum, New York, in press).