## New Variational Techniques for the 1snd States of Helium

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New variational techniques are described which yield a factor of 1000 improvement in accuracy for the energies of the  $1 \text{ snd } ^1D$  and  $^3D$  states of helium up to n=8. Convergence to better than  $\pm 10 \text{ kHz}$  is obtained, making possible high-precision comparisons with experiment for fine structure and singlet-triplet splittings. The comparisons are sensitive to QED, relativistic-recoil, and second-order mass-polarization corrections.

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The calculation of precise eigenvalues for the higherlying Rydberg states of helium has been a long-standing problem in the theory of atomic structure. The accurate variational calculations of Accad, Pekeris, and Schiff<sup>1</sup> are available for the low-lying S and P states, but the accuracy seriously deteriorates with increasing principal quantum number n. Several attempts have been made over the years to extend their type of calculations to Dand F states,<sup>2-4</sup> but the accuracy still falls far short of the  $\pm 100$  kHz ( $\pm 10^{-11}$  a.u.) or better needed to make a meaningful comparison with the large body of experimental measurements for transitions between Rydberg states.<sup>5-8</sup> The asymptotic calculations of Drachman<sup>9</sup> become useful for higher angular momentum, but there is as yet no overlap region where his results can be tested against the rigorous bounds provided by direct variational calculations.

The purpose of this Letter is to report new variational techniques which now make it possible to obtain nonrelativistic eigenvalues accurate to better than  $\pm 10$  kHz. As a first step, results will be given for the *D* states up to n=8. The eigenvalues show convergence to about three more significant figures than those recently reported by Kono and Hattori.<sup>4</sup> Relativistic, mass-polarization, and QED corrections are also included, and the final results

are compared with experimental energy splittings.

One can take advantage of the near screened-hydrogenic nature of Rydberg states by writing the nonrelativistic Hamiltonian in the form  $H = H_0 + V$ , where (in atomic units)

$$H = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - Z/r_1 - (Z-1)/r_2, \qquad (1)$$

$$V = 1/r_{12} - 1/r_2, \tag{2}$$

and Z-1 is the screened nuclear charge. (The coordinates  $r_1$  and  $r_2$  in  $H_0$  and V are interchanged when operating on exchange terms.) The eigenvalue problem

$$H_0\psi_0(1snd) = E_0\psi_0(1snd)$$
(3)

can of course be solved exactly, and the eigenvalues  $E_0 = -2 - 1/(2n^2)$  give correctly the first five or six figures of the true energy *E*. The strategy is, therefore, to include  $\psi_0(1snd)$  in the variational basis set and to subtract out explicitly the  $E_0$  contribution, so that the variational principle applied to  $H - E_0$  yields directly the correction to  $E_0$ . The final results would be the same without the subtraction, but this procedure helps to preserve numerical precision.

The variational trial function itself is written in the generalized form

$$\psi(\mathbf{r}_{1},\mathbf{r}_{2}) = a_{0}\psi_{0}(\mathbf{r}_{1},\mathbf{r}_{2}) + \sum_{i,j,k} a_{ijk}r_{1}^{i}r_{2}^{j}r_{12}^{k}\exp(-\alpha_{1}r_{1} - \beta_{1}r_{2})Y_{0,2,2}^{M}(\hat{\mathbf{r}}_{1},\hat{\mathbf{r}}_{2}) + \sum_{i,j,k} b_{ijk}r_{1}^{i}r_{2}^{j}r_{12}^{k}\exp(-\alpha_{2}r_{1} - \beta_{2}r_{2})Y_{0,2,2}^{M}(\hat{\mathbf{r}}_{1},\hat{\mathbf{r}}_{2}) + \sum_{i,j,k} c_{ijk}r_{1}^{i}r_{2}^{j}r_{12}^{k}\exp(-\alpha_{3}r_{1} - \beta_{3}r_{2})Y_{1,1,2}^{M}(\hat{\mathbf{r}}_{1},\hat{\mathbf{r}}_{2}), \quad (4)$$

where the  $Y_{l_1,l_2,L}^{M}(\hat{\mathbf{r}}_1,\hat{\mathbf{r}}_2)$  are the usual vector-coupled products of spherical harmonics with angular momenta  $l_1$  and  $l_2$ . In addition to  $\psi_0(1snd)$ , the above contains two sets of sd-type functions with different nonlinear parameters  $(\alpha_1,\beta_1)$  and  $(\alpha_2,\beta_2)$ . The doubling of sd-type terms is important because the problem inherently contains two distance scales—one for the inner electron and one for the outer electron. Kono and Hattori also recognized this point, but their restrictions on the basis set greatly limit the accuracy of the results.

Finally, the energy is optimized with respect to all six nonlinear parameters  $(\alpha_i, \beta_i, i = 1-3)$  in (4). This can be efficiently accomplished by the analytical calculation of the derivatives  $\partial E/\partial \alpha_i$  and  $\partial E/\partial \beta_i$ , where

$$E = E_0 + \langle \psi | H - E_0 | \psi \rangle / \langle \psi | \psi \rangle, \tag{5}$$

and by the location of the zero's of the derivatives by means of Newton's method. In the above,  $\psi$  is the trial

wave function optimized with respect to the linear variational parameters in (4) for a given set of values for the  $\alpha_i, \beta_i$ 's. The linear optimization is accomplished by a fast inverse iteration method in place of matrix diagonalization. The result is that  $\alpha_1 \simeq \alpha_2 \simeq 2$  and  $\beta_1 \simeq 1/n$ , while  $\beta_2$ ,  $\alpha_3$ , and  $\beta_3$  range between 1 and 2 depending on the state and the number of terms in the basis set. The details will be described more fully in a future publication.

As a typical example, Table I shows how the nonrelativistic eigenvalues converge with the size of the basis set for the 1s5d  $^1D$  and  $^3D$  states. All terms are included in (4) such that  $i+j+k \le N+2$ , except that  $k \le 4$  (or  $k \le 2$  for the largest two basis sets) in the first summation. This truncation raises the energies by less than  $10^{-13}$  a.u. Also, terms with i > j are omitted from the third summation (the pp' terms) in order to avoid near linear dependence in the basis set. The largest 613-term basis set corresponds to N=10, with 166, 286, and 161 terms in the three summations of Eq. (4). The present 145-term calculation already exceeds the accuracy of Kono and Hattori's largest 293-term result. All of the eigenvalues studied up to n=8 have converged to within a few parts in  $10^{13}$ .

Several small corrections to the eigenvalues must be included before a detailed comparison with experiment becomes meaningful, and are as follows.

(1) Mass-polarization corrections.— These were obtained by the explicit inclusion of the  $(\mu/M)\nabla_1 \cdot \nabla_2$  mass-polarization operator in the Hamiltonian, and recalculating the eigenvalues (with reoptimization of the nonlinear parameters). The results for the 1s 3d states can be expressed in the form

$$\Delta E_{MP}(3^{1}D) = -2.493980 \times 10^{-4} (\mu/M) - 5.7186 \times 10^{-2} (\mu/M)^{2} \text{ a.u.}$$
$$\Delta E_{MP}(3^{3}D) = 2.5334 \times 10^{-5} (\mu/M) - 5.482 \times 10^{-2} (\mu/M)^{2} \text{ a.u.}$$

For  ${}_{2}^{4}$ He,  $\mu/M = 1.3707458 \times 10^{-4}$  and  $\mu$  is the reduced electron mass. Since the coefficients of all the odd terms are small, higher-order corrections are negligible. It is particularly significant that for the  $3 {}^{3}D$  state, the second-order  $(\mu/M)^{2}$  term is nearly as large as the first-order term. The mass-polarization corrections are therefore quite different from those of Kono and Hattori since they only included the first-order term as a perturbation.

(2) Relativistic corrections.—The corrections of  $O(\alpha^2 Z^2)$  were calculated by the evaluation of matrix elements of the standard terms  $H_1, H_2, \ldots, H_5$  in the Breit interaction.<sup>10</sup> The spin-independent terms  $H_1+H_2$  agree with the figures quoted by Kono and Hattori for the  $n^3D$  states, but differ substantially for the  $n^1D$ 

states. For example, for the states  $3 {}^{1}D$  and  $8 {}^{1}D$ ,  $\langle H_{1} + H_{2} \rangle = -0.028 3872(2)$  cm<sup>-1</sup> and -0.003 25604(1) cm<sup>-1</sup>, while their values are -0.0293(3) and -0.003 32 cm<sup>-1</sup>, respectively. This accounts for most of the difference in the final results, and verifies the conclusion of Martin<sup>11</sup> that Kono and Hattori's energies for the  $n {}^{1}D$  states are too low. Anomalous magneticmoment and singlet-triplet mixing corrections are also included.

(3) QED corrections.—As in previous work,<sup>12</sup> the QED energy shift is taken to be the one-electron energy shift corrected for the electron density at the nucleus, together with explicit two-electron terms dependent on  $\langle \delta(\mathbf{r}_{12}) \rangle$  and Q. In this approximation, the energy shift is

$$\Delta E_L = \frac{4}{3} Z \alpha^3 \{ \ln(Z\alpha)^{-2} + \ln[Z^2 \mathcal{R}/\epsilon(nLS)] + \frac{19}{30} + 3\pi Z \alpha (\frac{427}{384} - \frac{1}{2} \ln 2) + (\alpha/\pi) 0.4042 \} \langle \delta(\mathbf{r}_1) + \delta(\mathbf{r}_2) \rangle + \alpha^3 (\frac{14}{3} \ln \alpha + \frac{164}{15}) \langle \delta(\mathbf{r}_{12}) \rangle - \frac{14}{3} \alpha^3 Q, \quad (6)$$

| N                             | Number of terms | 5 <sup>1</sup> D | $5 \ ^{3}D$    |
|-------------------------------|-----------------|------------------|----------------|
| 4                             | 92              | -1.583 505 18    | -2.10265751    |
| 5                             | 145             | -1.58360396      | -2.10273633    |
| 6                             | 214             | -1.58361290      | -2.10274225    |
| 7                             | 300             | -1.58361502      | -2.10274424    |
| 8                             | 405             | -1.58361578      | -2.10274459    |
| 9                             | 481             | -1.58361590      | -2.10274464    |
| 10                            | 613             | -1.58361596      | -2.10274466    |
| Extrapolation                 |                 | -1.58361599(3)   | -2.10274467(1) |
| Kono and Hattori <sup>a</sup> |                 | -1.5837(1)       | -2.1028(1)     |

TABLE I. Nonrelativistic energies of the 1s5d <sup>1</sup>D and <sup>3</sup>D states for infinite nuclear mass, relative to the screened-hydrogenic energy  $E_0 = -101/50$  a.u. (units are  $10^{-5}$  a.u.).

<sup>a</sup>Reference 4.

(7)

with

$$\ln \frac{\epsilon(nLS)}{Z^2 \mathcal{R}} = \ln \frac{\epsilon(1s)}{Z^2 \mathcal{R}} + \frac{1}{n^3} \ln \frac{\epsilon(nl)}{Z^2 \mathcal{R}}, \quad Q = \frac{1}{4\pi} \lim_{a \to 0} \langle r_{12}^{-3}(a) + 4\pi(\gamma + \ln a)\delta(\mathbf{r}_{12}) \rangle.$$

Here,  $\gamma$  is Euler's constant,  $\mathcal{R}$  is the Rydberg constant, a is the radius of a sphere centered at  $r_{12} = 0$ , which is excluded from the integration over  $r_{12}$ , and the hydrogenic Bethe logarithms  $\ln \epsilon(nl)$  are from Klarsfeld and Maquet.<sup>13</sup> The total energy shifts, relative to the He<sup>+</sup>(1s) energy shift, are -10.962 and -13.641 MHz for the 1s 3d<sup>1</sup>D and <sup>3</sup>D states, respectively. The two-electron parts [the last two terms of Eq. (6)] are -2.499 and -2.439 MHz.

(4) Relativistic-recoil corrections.—Corrections of order  $(m/M)a^2Z^2$  come from finite-nuclear-mass corrections to the Breit operator, and cross terms involving the Breit operator and mass-polarization corrections to the wave functions. If the conversion factor  $2\mathcal{R}_M = 2(\mu/m) \times \mathcal{R}_{\infty}$  is used to convert the Breit interaction matrix elements from atomic units to megahertz, then, following Stone<sup>14</sup> and Douglas and Kroll,<sup>15</sup> the finite-mass corrections are

$$\Delta E_{\rm RR} = \Delta_1 + \Delta_2 + \Delta_X - (m/M) [3H_1 + 2(H_2 + H_{3,\rm soo} + H_4 + H_5)]$$

where

$$\Delta_{1} = \sum_{k \neq l} \frac{Ze^{2}}{mMc^{2}} r_{k}^{-3} \mathbf{r}_{k} \cdot \mathbf{p}_{l} \cdot \mathbf{s}_{k},$$
  
$$\Delta_{2} = \sum_{k,l} \frac{Ze^{2}}{2mMc^{2}} (r_{k}^{-1} \mathbf{p}_{k} \cdot \mathbf{p}_{l} + r_{k}^{-3} \mathbf{r}_{k} \mathbf{r}_{k} : \mathbf{p}_{k} \mathbf{p}_{l})$$
  
$$\Delta_{X} = \langle \psi_{\mathrm{MP}} \mid \sum_{i} H_{i} \mid \psi_{\mathrm{MP}} \rangle - \langle \psi \mid \sum_{i} H_{i} \mid \psi \rangle.$$

 $\psi_{MP}$  is the wave function with mass-polarization corrections included, and  $H_1, \ldots, H_5$  are the Breit operators as defined by Bethe and Salpeter, <sup>10</sup> with  $H_{3,soo}$  being the spin-other-orbit part of  $H_3$ . The values of  $\Delta E_{RR}$  for the  $1s 3d {}^1D_2$ ,  ${}^3D_1$ ,  ${}^3D_2$ , and  ${}^3D_3$  states are 0.052, -0.427, -0.059, and -0.011 MHz, respectively. The corresponding  $\Delta_X$  contributions to  $\Delta E_{RR}$  are 0.568, 0.605, 0.491, and 0.323 MHz. These corrections are large enough to be observable in the triplet splittings for n=3.

For higher *n*, they decrease approximately in proportion to  $n^{-3}$ .

Table II summarizes the calculated ionization energies for the 1*snd* states up to n=8. The errors represent the estimated degree of convergence of the calculation with no allowance for higher-order uncalculated terms. The largest of these is the order- $a^4Z^6$  relativistic correction. Its magnitude as estimated from the leading hydrogenic term<sup>16</sup> with a screened nuclear charge is less than 0.1 MHz for n=3, and decreases in proportion to  $n^{-3}$ . For n=3, the  ${}^{3}D_{1}$ - ${}^{3}D_{3}$  splitting from Table II is 1400.44 MHz, in agreement with the average experimental value 1400.66(23) MHz adopted by Sansonetti and Martin.<sup>7</sup> However, the calculated  ${}^{3}D_{1}$ - ${}^{3}D_{2}$  splitting of 1325.03 MHz is slightly larger than their recommended value of 1324.6(3) MHz.

TABLE II. Ionization energies (in megahertz) of the 1*snd* states, relative to the screenedhydrogenic ionization energy  $\mathcal{R}_M/n^2$ . The first entry of each pair is the nonrelativistic value, and the second includes the other corrections discussed in the text. [The small corrections  $\Delta_X$ and terms of order  $(\mu/M)^2$  are included only for n=3.]  $\mathcal{R}_M=3289390995$  MHz and  $\alpha^{-1}=137.03596$  are used in all conversions.

| n | <sup>1</sup> D <sub>2</sub> | ${}^{3}D_{1}$   | ${}^{3}D_{2}$   | ${}^{3}D_{3}$   |
|---|-----------------------------|-----------------|-----------------|-----------------|
| 3 | 428 787.225                 | 531 262.287     | 531 262.287     | 531 262.287     |
|   | 429 856.290(6)              | 531 000.055(6)  | 532 325.085(6)  | 532 400.500(6)  |
| 4 | 196351.505(8)               | 255 569.247(3)  | 255 569.247(3)  | 255 569.247(3)  |
|   | 196992.539(40)              | 255 604.729(20) | 256 159.891(20) | 256 195.865(20) |
| 5 | 104 182.643(2)              | 138334.988(1)   | 138334.988(1)   | 138334.988(1)   |
|   | 104 568.332(6)              | 138400.376(3)   | 138683.902(3)   | 138703.097(3)   |
| 6 | 61436.187(1)                | 82409.538(1)    | 82409.538(1)    | 82409.538(1)    |
|   | 61681.186(5)                | 82465.979(2)    | 82629.841(2)    | 82641.171(2)    |
| 7 | 39122.866(1)                | 52790.270(1)    | 52790.270(1)    | 52790.270(1)    |
|   | 39286.844(1)                | 52834.297(2)    | 52937.405(2)    | 52944.620(2)    |
| 8 | 26 397.781(1)               | 35753.782(1)    | 35753.782(1)    | 35753.782(1)    |
|   | 26 512.465(1)               | 35787.587(2)    | 35856.624(2)    | 35861.492(2)    |

The  ${}^{3}D_{1} {}^{3}D_{3}$  splittings have also been calculated by Martinis and Pilkuhn<sup>17</sup> using a relativistic polarization model. Agreement with their results is good for n=3 and 4, but deteriorates with increasing *n*. For example at n=8, Martinis and Pilkuhn obtained 73.58 MHz, while the value from Table II is 73.90 MHz in agreement with the experimental value 74.02  $\pm$  0.13 MHz.<sup>5</sup>

For the singlet-triplet splittings  $n^{1}D_{2}$ - $n^{3}D_{cg}$ , the values for n=7 and 8 are 13633.31 and 9332.62 MHz, in excellent agreement with the measured values 13633.3(2) and 9332.67(8) MHz, respectively.<sup>5</sup> However, there is a significant discrepancy for n=3. The calculated value of 102239.0 MHz lies two error bars higher than the 102233(3) MHz determined indirectly by Sansonetti and Martin. This is more than twice the entire QED contribution of 2.68 MHz. A genuine discrepancy this large, which varies as  $n^{-3}$ , would destroy the agreement at n=8. It therefore seems likely that the experimental determination is too small by about 6 MHz.

This work establishes the non-QED part of the *D*-state energies for helium to about the same accuracy as for the ground state.<sup>18</sup> Results of similar accuracy have also been obtained by the same methods for the low-lying *S* and *P* states, as will be described in a future publication. The variational techniques described here therefore appear to provide a general method for the calculation of two-electron energies to an accuracy of about one part in  $10^{13}$  with a reasonable amount of computational effort. This will open the way to a wide range of new highprecision comparisons between theory and experiment.

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<sup>1</sup>Y. Accad, C. L. Pekeris, and B. Schiff, Phys. Rev. A **4**, 516 (1971); K. Frankowski, Phys. Rev. **160**, 1 (1967).

<sup>2</sup>P. Blanchard and G. W. F. Drake, J. Phys. B 6, 2495 (1973).

<sup>3</sup>J. S. Sims, D. R. Parmer, and J. M. Reese, J. Phys. B 15, 327 (1982).

<sup>4</sup>A. Kono and S. Hattori, Phys. Rev. A 34, 1727 (1986).

<sup>5</sup>J. W. Farley, K. B. MacAdam, and W. H. Wing, Phys. Rev. A **20**, 1754 (1979).

<sup>6</sup>D. R. Cok and S. R. Lundeen, Phys. Rev. A **19**, 1830 (1979), and **24**, 3283 (1981); E. A. Hessels, W. G. Sturrus,

S. R. Lundeen, and D. R. Cok, Phys. Rev. A 35, 4489 (1987).

<sup>7</sup>C. J. Sansonetti and W. C. Martin, Phys. Rev. A **29**, 159 (1984); W. C. Martin, Phys. Rev. A **29**, 1883 (1984).

<sup>8</sup>L. Hlousek, S. A. Lee, and W. M. Fairbank, Jr., Phys. Rev. Lett. **50**, 328 (1983).

 ${}^{9}$ R. J. Drachman, Phys. Rev. A **31**, 1253 (1985), and earlier references herein.

<sup>10</sup>H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Springer-Verlag, Berlin, 1957).

<sup>11</sup>W. C. Martin, Phys. Rev. A (to be published).

<sup>12</sup>G. W. F. Drake and A. J. Makowski, J. Phys. B 18, L103 (1985).

<sup>13</sup>S. Klarsfeld and A. Maquet, Phys. Lett. **43B**, 201 (1973).

<sup>14</sup>A. P. Stone, Proc. Phys. Soc., London **81**, 868 (1963).

<sup>15</sup>M. Douglas and N. M. Kroll, Ann. Phys. (N.Y.) **82**, 89 (1974).

<sup>16</sup>G. W. F. Drake, Nucl. Instrum. Methods **B9**, 465 (1985).
<sup>17</sup>M. Martinis and H. Pilkuhn, J. Phys. B **15**, 1797 (1982).

<sup>18</sup>D. E. Freund, B. D. Huxtable, and J. D. Morgan, III, Phys. Rev. A **29**, 980 (1984).