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# HIGH PRECISION VARIATIONAL CALCULATIONS FOR THE $1s^2\,{}^1S$ STATE OF $H^-$ AND THE $1s^2\,{}^1S$, $1s2s\,{}^1S$ AND $1s2s\,{}^3S$ STATES OF HELIUM

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High precision variational eigenvalues are presented for the $1s^2\,{}^1S$ state of $H^-$, and the $1s^2\,{}^1S$, $1s2s\,{}^1S$ and $1s2s\,{}^3S$ states of helium, together with relativistic, mass polarization and relativistic recoil corrections. In addition to the nonrelativistic energy, all corrections of order $\alpha^2$, $\mu/M$ $(\mu/M)^2$ and $\alpha^2\mu/M$ are calculated to an accuracy of better than $10^{-6}$ cm$^{-1}$. Previous results of similar accuracy are available for the $1snd\,{}^1D$ and ${}^3D$ states up to $n=8$. A comparison with the high precision $1s2s\,{}^3S_1$–$1snd\,{}^3D_1$ transition frequency measurements of Hlousek et al. indicates that the known quantum electrodynamic (Lamb shift) contribution of $-0.13488$ cm$^{-1}$ to the ionization energy of the $1s2s\,{}^3S_1$ state is too small in magnitude by 0.00048(6) cm$^{-1}$. A discrepancy of this size can reasonably be accounted for by as yet uncalculated contributions to the two-electron Lamb shift.

## 1. Introduction

The accuracy of measurements of the helium $1s2s\,{}^3S_1$–$1snd\,{}^3D_1$ transition wavelengths for $n=4$ and 5 by Hlousek et al. [1] is sufficient to determine the Lamb shift of the $1s2s\,{}^3S_1$ state to a precision of about 6 parts in $10^5$. However, the interpretation of the experimental results has been hampered by an insufficiently accurate knowledge of the nonrelativistic energies of the states, together with a number of other non-QED corrections.

We have recently described some new variational techniques for two-electron atoms [2] in which a Hylleraas-type correlated basis set is "doubled" by including each combination of powers of $r_1$, $r_2$ and $r_{12}$ $(r_{12}=|r_1-r_2|)$ twice with different exponential nonlinear parameters, along with the exact screened hydrogenic wave function. A complete optimization is then performed with respect to all the nonlinear parameters, as described below. The basis set was originally designed with applications to high-lying Rydberg states in mind, where it gives convergence to a few parts in $10^{13}$ for the D-states up to $n=8$ [2]. However, tests of the method for the low-lying S and P states indicate that it works extremely well here also. The S-state results presented in this paper significantly improve on the accuracy of the older tabulations by Accad et al. [3], and at least match the accuracy of more recent work by Freund et al. [4] and Baker et al. [5] on the ground state. The results enable one to extract the QED and higher-order relativistic effects from the experimental data to the full extent of the experimental precision.

## 2. Computational procedure

In this section, the variational basis set is described, and the method for optimizing the nonlinear parameters is briefly outlined.

In the double basis set method, the trial function is written in the form $\Psi_{tr}=\Psi(r_1, r_2)\pm\Psi(r_2, r_1)$ where, for S-states

$$\Psi(r_1, r_2)=a_0\Psi_0(1s, ns)+\sum_{i,j,k} a_{ijk} r_1^i r_2^j r_{12}^k\, e^{-\alpha_1 r_1-\beta_1 r_2} + \sum_{i,j,k} b_{ijk} r_1^i r_2^j r_{12}^k\, e^{-\alpha_2 r_1-\beta_2 r_2} \tag{1}$$

and $\Psi_0(1s, ns)$ is the screened hydrogenic wave function with nuclear charges $Z$ and $Z-1$ for the two electrons. This choice is particularly appropriate for Rydberg states, but it does no harm for low-lying states. All terms are included in (1) such that $i+j+k\le N$, except that the $i=j=k=0$ term is omitted from the first summation so as not to (nearly) duplicate $\Psi_0$ (1s, $ns$). (For $H^-$, the $\Psi_0$(1s, 1s) term is omitted instead since $Z-1=0$ for this case.) Also terms with $i>j$ are omitted because this would correspond to a further doubling of the basis set with $\alpha_t$ and $\beta_t$ $(t=1, 2)$ interchanged.

The optimization of the $\alpha$'s and $\beta$'s is efficiently accomplished by calculating analytically the derivatives

$$\frac{\partial E}{\partial\alpha_t}=-2\langle\Psi_{tr}|H-E|r_1\Psi(r_1, r_2;\ \alpha_t) \pm r_2\Psi(r_2, r_1;\ \alpha_t)\rangle, \tag{2}$$

$$\frac{\partial E}{\partial\beta_t}=-2\langle\Psi_{tr}|H-E|r_2\Psi(r_1, r_2;\ \beta_t) \pm r_1\Psi(r_2, r_1;\ \beta_t)\rangle, \tag{3}$$

where $\langle\Psi_{tr}|\Psi_{tr}\rangle=1$ and $\Psi(r_1, r_2;\ \alpha_t)$ denotes the terms in (1) which depend explicitly on $\alpha_t$. There is no contribution to the derivatives from the implicit depen-

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dence of $E$ on $\alpha_t$ (or $\beta_t$) through the linear coefficients $a_{ijk}$ and $b_{ijk}$ in (1) because the energy is stationary in first order with respect to variations of the linear coefficients. The procedure followed was to estimate the second derivatives by differencing and locate the zero's of the first derivatives by Newton's method. Provided that the initial $\alpha$'s and $\beta$'s are chosen close to a minimum, the procedure converges in a few iterations, particularly for large basis sets.

## 3. Nonrelativistic eigenvalues

Table 1 shows the convergence of the eigenvalues as the basis set is enlarged for the $1s^2\,{}^1S$ state of $H^-$ and He. Since the ratios of successive differences are approximately constant for large basis sets, the extrapolated energy is obtained by assuming that higher order differences continue decreasing as a geometric series. The uncertainty is conservatively estimated as the entire amount of the extrapolation from the largest $N = 13$ calculation to $N = 14$.

For $H^-$, the present 190-term calculation matches the accuracy of Frankowski and Pekeris's 246-term result, and the ultimate uncertainty of $1 \times 10^{-13}$ a.u. is better than theirs by a factor of about 2000. The eigenvalue agrees to about 14 figures with the value obtained by Baker et al. [5] by summing a $1/Z$ expansion perturbation series to high order. For the ground state of helium, the ultimate convergence of $0.3 \times 10^{-13}$ a.u. is about the same as obtained by Freund et al. [4]. They reached this level of accuracy with only 230 terms by including logarithmic terms in the basis set. The good agreement indicates that logarithmic terms hasten the rate of convergence, but any *essential* contribution to the energy from logarithmic terms is less than $10^{-13}$ a.u.

Analogous results are given in table 1 for the excited S-states of helium. Although the $1s2s\,{}^1S$ state is somewhat more slowly convergent than the ground state, the $1s2s\,{}^3S$ state is much more rapidly convergent with an ultimate uncertainty of only $3 \times 10^{-16}$ a.u. This is now the most accurately known nonrelativistic energy for any two-electron state. For the smaller basis sets, the results are comparable in accuracy to those obtained by Frankowski [6] using logarithmic and hyperbolic functions. Double basis sets have also been used by Kono and Hattori [7], but the auxiliary restrictions they place on the basis set greatly limit the accuracy of their results.

It is also of interest to compare the small 44 and 6 term results in table 1 with the rapidly convergent integral-transform wave functions of Thakkar and Smith [8], in which the expansion terms are all of the form $\exp(-\alpha_t r_1 - \beta_t r_2 - \gamma_t r_{12})$. For the ground state of He, the present results are only slightly inferior to theirs for basis sets of about the same size, while for the excited states, the present results appear to be slightly better (i.e. lower energies). For $H^-$, the 68-term value of $-0.527750974$ from table 1 lies lower than their 60-term result of $-0.52775094$. The present wave functions therefore achieve about the same degree of "compactness" as theirs.

Table 1
Convergence of the nonrelativistic eigenvalues for infinite nuclear mass. $N$ is the basis set index such that $i + j + k \leq N$ in eq. (1). Numbers in brackets indicate the uncertainties in the final figures quoted

| $N$ | No. of terms | $H^-$ ($1s^2\,{}^1S$) | He ($1s^2\,{}^1S$) |
|---|---|---|---|
| 4 | 44 | −0.5277507368881 | −2.9037241310211 |
| 5 | 68 | −0.5277509742432 | −2.9037243515899 |
| 6 | 100 | −0.5277510091265 | −2.9037243739261 |
| 7 | 140 | −0.5277510153341 | −2.9037243766000 |
| 8 | 190 | −0.5277510162993 | −2.9037243769652 |
| 9 | 250 | −0.527751016497397 | −2.903724377020902 |
| 10 | 322 | −0.527751016534555 | −2.903724377031537 |
| 11 | 406 | −0.527751016541944 | −2.903724377033508 |
| 12 | 504 | −0.527751016543806 | −2.903724377033960 |
| 13 | 616 | −0.527751016544203 | −2.903724377034073 |
|  | extrap. | −0.527751016544306(85) | −2.903724377034105(28) |
|  |  | He ($1s2s\,{}^1S$) | He ($1s2s\,{}^3S$) |
| 4 | 44 | −2.1459736210739 | −2.1752293689656 |
| 5 | 68 | −2.1459739982741 | −2.1752293766788 |
| 6 | 100 | −2.1459740362799 | −2.1752293780769 |
| 7 | 140 | −2.1459740447865 | −2.1752293782159 |
| 8 | 190 | −2.1459740458089 | −2.1752293782345 |
| 9 | 250 | −2.145974046004007 | −2.175229378236475 |
| 10 | 322 | −2.145974046044291 | −2.175229378236747 |
| 11 | 406 | −2.145974046051233 | −2.1752293782367820 |
| 12 | 504 | −2.145974046053633 | −2.1752293782367893 |
| 13 | 616 | −2.145974046054143 | −2.1752293782367907 |
|  | extrap. | −2.14597404605428(11) | −2.1752293782367910(3) |

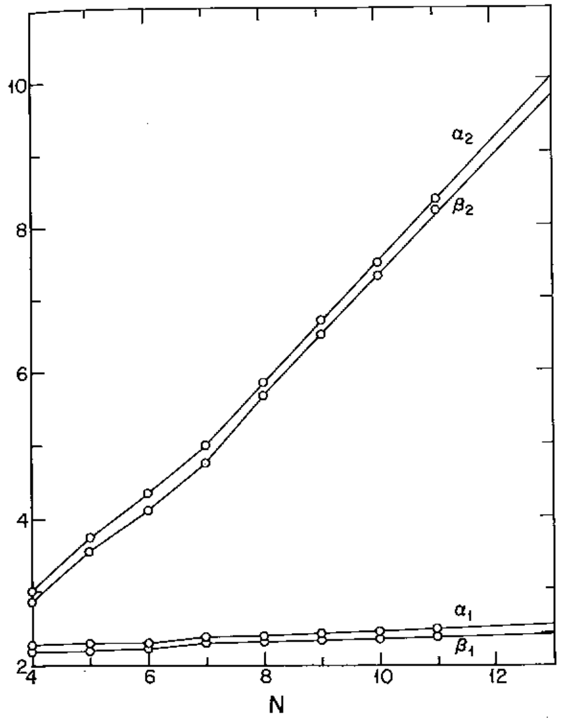

Fig. 1. Variation of the optimized nonlinear parameters in eq. (1) with the basis set index $N$ for the $1s^2\,{}^1S$ state of helium.

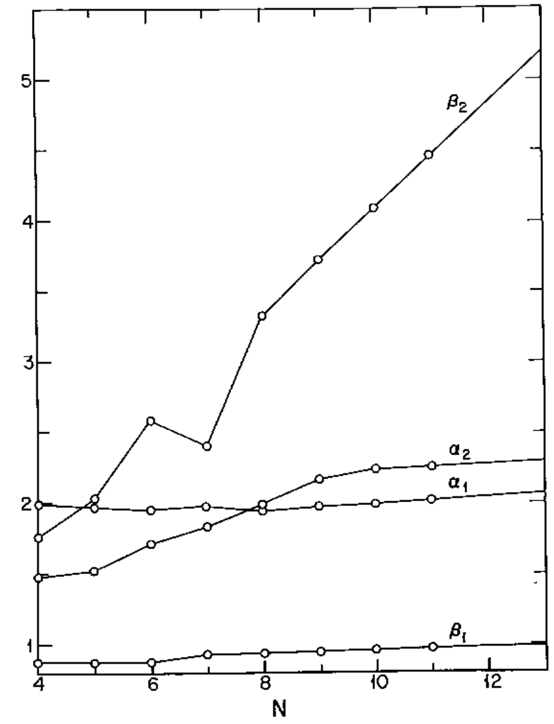

Fig. 2. Variation of the optimized nonlinear parameters in eq. (1) with the basis set index $N$ for the $1s2s\,{}^3S$ state of helium.

The variation of the optimum non-linear parameters with the basis set index $N$ is illustrated in figs. 1 and 2 for the $1s^2\,{}^1S$ and $1s2s\,{}^3S$ states of helium. The values of $\alpha_1$ and $\beta_1$ are close to the screened hydrogenic values, while $\alpha_2$ and/or $\beta_2$ increase almost linearly with $N$ such that the function $r^N e^{-\beta r}$ peaks at about the same value of $r$. The linear rise in $\beta_2$ ensures that the terms in the doubled basis set do not approach linear dependence as $N$ increases. The $\alpha_1$, $\beta_1$ terms in (1) are apparently describing the physically expected long range behaviour of the wave function, while the $\alpha_2$, $\beta_2$ terms are describing complex inner correlation effects. However, there are multiple roots corresponding approximately to pairwise interchanges of the $\alpha_t$, $\beta_t$, with further multiplicities in some cases. The four-dimensional energy surface generated by varying the $\alpha$'s and $\beta$'s appears to have a rather complicated structure, and one must be careful to choose the lowest numerically stable root for a small basis set and then follow it by extrapolation to larger basis sets. For example in fig. 2, the anomaly in $\beta_2$ at $N = 7$ appears to be related to the appearance of a second set of numerically unstable roots with $\alpha_2 \simeq \beta_2$ for $N > 7$ which lie midway between the $\alpha_2$, $\beta_2$ lines shown in the figure.

## 4. Small corrections

Since second-order mass polarization effects are important for calculations of this accuracy, the eigenvalues were recalculated with the $(\mu/M)\boldsymbol{p}_1 \cdot \boldsymbol{p}_2$ mass polarization operator included explicitly in the Hamiltonian. The resulting energy shifts can be expressed in the form

$$\Delta E_M(H^-\ 1\,{}^1S) = 0.03287978125(\mu/M) - 0.059779493(\mu/M)^2$$

$$\Delta E_M(\mathrm{He}\ 1\,{}^1S) = 0.1590694751(\mu/M) - 0.47039190(\mu/M)^2$$

$$\Delta E_M(\mathrm{He}\ 2\,{}^1S) = 0.009503864419(\mu/M) - 0.135277(\mu/M)^2$$

$$\Delta E_M(\mathrm{He}\ 2\,{}^3S) = 0.007442130706(\mu/M) - 0.0574958(\mu/M)^2$$

in units of $2R_M$, where $R_M = [1-(\mu/M)]R_\infty$ and $\mu$ is the reduced electron mass $mM/(m+M)$. For $^4$He, $(\mu/M) = 1.370745633 \times 10^{-4}$, and for $H^-$, $(\mu/M) = 5.44320567 \times 10^{-4}$. The leading coefficient above is $\langle \boldsymbol{p}_1 \cdot \boldsymbol{p}_2 \rangle$ calculated for infinite nuclear mass, and the next coefficient is obtained by subtracting the leading term from the directly calculated total energy shift due to mass polarization. The above formulas therefore exactly reproduce the directly calculated energies for the given values of $\mu/M$. Since all the odd coefficients vanish in the absence of electron correlation, they are all small for the excited states in comparison with the even terms, and hence terms beyond $(\mu/M)^2$ are negligible for these states. For the ground states, the coefficients of $(\mu/M)^2$ may contain small contributions from higher order terms due to the subtraction procedure used to calculate them.

The remaining corrections included in this work are relativistic, relativistic recoil, Lamb shift and finite nuclear size effects. In the notation of Bethe and Salpeter [9], the relativistic corrections are

$$\Delta E_{\rm rel} = \left\langle \Psi \left| \sum_{i=1}^{5} H_i \right| \Psi \right\rangle, \tag{4}$$

where

$$H_1 = -\frac{\alpha^2}{8}\left(p_1^4 + p_2^4\right), \tag{5}$$

$$H_2 = -\frac{\alpha^2}{2r_{12}}\left[\boldsymbol{p}_1 \cdot \boldsymbol{p}_2 + r_{12}^{-2}\boldsymbol{r}_{12} \cdot (\boldsymbol{r}_{12} \cdot \boldsymbol{p}_1)\boldsymbol{p}_2\right], \tag{6}$$

$$H_4 = \pi\alpha^2\left[Z\delta(\boldsymbol{r}_1) - \delta(\boldsymbol{r}_{12})\right] \tag{7}$$

and $H_3$ and $H_5$ are the spin–orbit and spin–spin interactions. For S-states, $H_3$ does not contribute and $H_5$ reduces to

$$H_5 = 2\pi\alpha^2\delta(\boldsymbol{r}_{12}). \tag{8}$$

For the D states, anomalous magnetic moment corrections are included in the spin-dependent parts of the $\Delta E_{\rm rel}$ as described in [2].

The relativistic recoil terms are finite mass corrections to the Breit interaction. If the reduced mass Rydberg $R_{\rm M}$ is used to convert all quantities from a.u. to cm$^{-1}$, then, following Stone [10]

$$\Delta E_{\rm RR} = (\Delta E_{\rm RR})_{\rm M} + (\Delta E_{\rm RR})_{\rm X} \tag{9}$$

where

$$(\Delta E_{\rm RR})_{\rm M} = \Delta_1 + \Delta_2 - \frac{m}{M}\left[3H_1 + 2(H_2 + H_{3,\rm soo} + H_4 + H_5)\right] \tag{10}$$

with

$$\Delta_1 = \sum_{k \neq l}\left(Ze^2/mMc^2\right) r_k^{-3} \boldsymbol{r}_{1k} \times \boldsymbol{p}_l \cdot \boldsymbol{s}_k \tag{11}$$

$$\Delta_2 = -\sum_{k,l}\left(Ze^2/2mMc^2\right) \times \left[r_k^{-1}\boldsymbol{p}_k \cdot \boldsymbol{p}_l + r_k^{-3}\boldsymbol{r}_k \cdot (\boldsymbol{r}_k \cdot \boldsymbol{p}_k)\boldsymbol{p}_l\right] \tag{12}$$

and

$$(\Delta E_{\rm RR})_{\rm X} = \left\langle \Psi_{\rm MP} \left| \sum_i H_i \right| \Psi_{\rm MP} \right\rangle - \left\langle \Psi \left| \sum_i H_i \right| \Psi \right\rangle. \tag{13}$$

$\Psi_{\rm MP}$ is the wave function with mass polarization corrections included. Thus $(\Delta E_{\rm RR})_{\rm X}$ takes into account the second order cross terms between the Breit interaction and the mass polarization operator.

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 $\langle \delta(\boldsymbol{r}_{12}) \rangle$ and $Q$. In this approximation, the energy shift is [11,12]

$$\Delta E_L = \Delta E_{L,1} + \Delta E_{L,2}, \tag{14}$$

where

$$\begin{aligned}\Delta E_{L,I} = \tfrac{4}{3}Z\alpha^3\Big\{&\ln(Z\alpha)^{-2} + \ln\left[Z^2\ {\rm Ryd}/\epsilon(nLS)\right] + \tfrac{19}{30} \\ &+ 3\pi Z\alpha\left(\tfrac{427}{384} - \tfrac{1}{2}\ln 2\right) + (Z\alpha)^2\Big[-\tfrac{3}{4}\ln^2(Z\alpha)^2 \\ &+ C_{61}\ \ln(Z\alpha)^2 + C_{60}\Big] \\ &+ \frac{\alpha}{\pi}0.4042\Big\}\langle \delta(\boldsymbol{r}_1) + \sigma(\boldsymbol{r}_2) \rangle\end{aligned} \tag{15}$$

$$\Delta E_{L,2} = \alpha^3\left(\tfrac{14}{3}\ln\alpha + \tfrac{164}{15}\right)\langle \delta(\boldsymbol{r}_{12}) \rangle - \tfrac{14}{3}\alpha^3 Q \tag{16}$$

and

$$Q = \frac{1}{4\pi}\lim_{a \to 0}\left\langle r_{12}^{-3}(a) + 4\pi(\gamma + \ln a)\delta(\boldsymbol{r}_{12}) \right\rangle. \tag{17}$$

Here, $\gamma$ is Euler's constant and $a$ is the radius of a sphere centered at $r_{12} = 0$ which is excluded from the integration over $r_{12}$. The Bethe logarithms are estimated from the screened hydrogenic form [13,14]

$$\ln\left[\epsilon(nLS)/Z^2\ {\rm Ryd}\right] = \ln\left[\epsilon_0(nLS)(Z-\sigma)^2/Z^2\ {\rm Ryd}\right] \tag{18}$$

where $\ln\epsilon_0(nLS)$ is determined from the hydrogenic Bethe logarithms according to [15,16]

$$\ln\epsilon_0(nLS) = \left[\ln\epsilon(1{\rm s}) + n^{-3}\ln\epsilon(nl)\right]/\left(1 + n^3\delta_{l,0}\right). \tag{19}$$

The hydrogenic Bethe logarithms are tabulated by Klarsfeld and Maquet [17]. The screening constants $\sigma$ in eq. (18) have been calculated by Goldman and Drake [13] for the low-lying S- and P-states from the leading terms in the $1/Z$ expansion of the two-electron Bethe logarithm. The final results for the S-states are

$$\ln\left[\epsilon(1\,^1{\rm S})/{\rm Ryd}\right] = \ln\left[19.7692669(Z - 0.00615)^2\right], \tag{20}$$

$$\ln\left[\epsilon(2\,^1{\rm S})/{\rm Ryd}\right] = \ln\left[19.3942687(Z + 0.02040)^2\right], \tag{21}$$

$$\ln\left[\epsilon(2\,^2{\rm S})/{\rm Ryd}\right] = \ln\left[19.3942687(Z + 0.01388)^2\right]. \tag{22}$$

The coefficients $C_{61}$ and $C_{60}$ in eq. (15) are weakly state dependent. The values of $C_{61}$ for the 1s and 2s states are 3.964530 and 4.347589 respectively [18]. In analogy with eq. (19) for the Bethe logarithm, the two-electron value for $C_{61}$ is taken to be

$$C_{61}(nLS) = \left[C_{61}(1{\rm s}) + n^{-3}C_{61}(nl)\right]/\left(l + n^{-3}\delta_{0,l}\right). \tag{23}$$

This gives 4.00709 for the 1s2s states. The state dependence of $C_{60}$ is not known, but it is expressed to be similarly small. The value $-24$ was used for both the 1s and 2s states [19,20].

The correction due to finite nuclear size is given in lowest order by

$$\Delta E_{\rm nuc} = \frac{2\pi Z(R/a_0)^2}{3}\langle \delta(\boldsymbol{r}_1) + \delta(\boldsymbol{r}_2) \rangle, \tag{24}$$

where $R$ is the root-mean-square radius of the nuclear charge distribution and $a_0$ is the Bohr radius. The values used were $R = 1.673$ fm for He [21] and $R = 0.862$ fm for $H^-$ [22].

The matrix elements needed to evaluate the above corrections are summarized in table 2. The final calculations were all performed in quadruple precision (approximately 32 decimal digits). A number of general formulas which are useful in the evaluation of the matrix elements for states of arbitrary angular momentum are given in ref. [23]. The matrix elements of $\delta(\boldsymbol{r}_1)$ were calculated by means of the global operator derived by Hiller et al. [24], with modifications arising from the $(\mu/M)\boldsymbol{p}_1 \cdot \boldsymbol{p}_2$ term in the Hamiltonian. The final result is

$$\begin{aligned}\langle \delta(\boldsymbol{r}_1) \rangle = \frac{1}{2\pi}\Big\langle &\frac{Z}{r_1^2} - \frac{1}{r_{12}^2}\frac{\partial r_{12}}{\partial r_1} - \frac{1}{r_1^3}l_1^2 \\ &+ \frac{\mu}{Mr_1}\Big[\nabla_1 \cdot \nabla_2 - \frac{1}{r_1^2}\boldsymbol{r}_1 \cdot (\boldsymbol{r}_1 \cdot \nabla_1)\nabla_2 \\ &- \frac{1}{r_1^2}\boldsymbol{r}_1 \cdot \nabla_2\Big]\Big\rangle.\end{aligned} \tag{25}$$

The operator in square brackets is the additional contribution due to $(\mu/M)\boldsymbol{p}_1 \cdot \boldsymbol{p}_2$. The last term is required to make the operator Hermitian. Compact general formulas for the evaluation of this and other terms in the Breit interaction will be given in a future publication. The use of eq. (25) accelerates the rate of convergence by about a factor of 20 relative to a direct evaluation of $\langle \delta(\boldsymbol{r}_1) \rangle$.

Table 2
Values for various matrix elements requires to calculate relativistic and QED corrections to the energy. Each quantity is expressed in the form $\langle T \rangle = \langle T_0 \rangle + \langle T_1 \rangle(\mu/M)$ a.u., where $\langle T_1 \rangle(\mu/M)$ is the change in the matrix element when the mass polarization term $\boldsymbol{p}_1 \cdot \boldsymbol{p}_2(\mu/M)$ is included explicitly in the Hamiltonian $H = -(\nabla_1^2 + \nabla_2^2)/2 - Z/r_1 - Z/r_2 + 1/r_{12}$

| Matrix element | $\langle T_0 \rangle$ | $\langle T_1 \rangle$ |
|---|---|---|
| | $H^-$ (1s$^2$ $^1$S) | |
| $\langle p_1^4 \rangle/4$ | 0.61563964(3) | −0.00063343(3) |
| $\langle H_2 \rangle/\alpha^2$ | −0.0088750223(2) | 0.0324809408(1) |
| $\pi\langle \delta(\boldsymbol{r}_1) \rangle$ | 0.516958096(1) | −0.02524237(1) |
| $\pi\langle \delta(\boldsymbol{r}_{12}) \rangle$ | 0.008601665(5) | −0.01127722(1) |
| $\Delta_2/(\alpha^2{\rm m}/M)$ | −1.01456268(1) | |
| $Q$ | 0.0078554(1) | |
| | He (1s$^2$ $^1$S) | |
| $\langle p_1^4 \rangle/4$ | 13.5220168(1) | −0.1758280(1) |
| $\langle H_2 \rangle/\alpha^2$ | −0.01390946907(4) | 0.638933826(2) |
| $\pi\langle \delta(\boldsymbol{r}_1) \rangle$ | 5.687631448(1) | −0.28647130(1) |
| $\pi\langle \delta(\boldsymbol{r}_{12}) \rangle$ | 0.33409386(4) | −0.0387070(1) |
| $\Delta_2/(\alpha^2 m/M)$ | −22.6482980(1) | |
| $Q$ | 0.0787238(1) | |
| | He (1s2s $^1$S) | |
| $\langle p_1^4 \rangle/4$ | 10.2796689(1) | 0.0200726(2) |
| $\langle H_2 \rangle/\alpha^2$ | −0.0092530465(6) | 0.142257377(1) |
| $\pi\langle \delta(\boldsymbol{r}_1) \rangle$ | 4.11379236(1) | −0.0012624(2) |
| $\pi\langle \delta(\boldsymbol{r}_{12}) \rangle$ | 0.02716989(3) | 0.00555329(2) |
| $\Delta_2/(\alpha^2 m/M)$ | −16.656864(1) | |
| $Q$ | 0.0054069(1) | |
| | He (1s2s $^3$S) | |
| $\langle p_1^4 \rangle/4$ | 10.45888519(1) | 0.01062391(4) |
| $\langle H_2 \rangle/\alpha^2$ | −0.001628430062(0) | 0.0235281977(0) |
| $\pi\langle \delta(\boldsymbol{r}_1) \rangle$ | 4.1480178287(5) | 0.006838839(2) |
| $\pi\langle \delta(\boldsymbol{r}_{12}) \rangle$ | 0.0 | 0.0 |
| $\Delta_2/(\alpha^2 m/M)$ | −16.905331(1) | |
| $Q$ | 0.003092499(1) | |

## 5. Results and discussion

The various contributions to the energy are summarized in tables 3 and 4 for the S and D states. Each quantity is given relative to the corresponding term for the He$^+$(1s) state so that its negative is a contribution to the ionization potential. All quantities have converged to at least the number of figures quoted.

Since the Lamb shifts for the D states are much

Table 3
Contributions to the S-state energies ($\mathrm{cm}^{-1}$), using $R_\infty = 109737.31569\ \mathrm{cm}^{-1}$ [25] and $\alpha^{-1} = 137.03596$. For He, $\mu/M = 1.370745633 \times 10^{-4}$ and $R_M = 109722.273495\ \mathrm{cm}^{-1}$. For $H^-$, $\mu/M = 5.44320567 \times 10^{-4}$ and $R_M = 109677.583412\ \mathrm{cm}^{-1}$. $\Delta E_M^{(1)}$ and $\Delta E_M^{(2)}$ are the first and second order mass polarization corrections given in section 4 of the text

| | $H^-$ ($1s^2\ {}^1S$) | He ($1s^2\ {}^1S$) | He (1s2s ${}^1S$) | He (1s2s ${}^3S$) |
|---|---|---|---|---|
| $E_{NR}$ | −6087.328864 | −198317.386523 | −32033.208409 | −38453.131527 |
| $\Delta E_M^{(1)}$ | 3.925830 | 4.784852 | 0.285879 | 0.223861 |
| $\Delta E_M^{(2)}$ | −0.003885 | −0.001940 | −0.000558 | −0.000237 |
| $\Delta E_{rel}$ | 0.304232 | 0.563780 | −0.399270 | −1.922044 |
| $(\Delta E_{RR})_M$ | −0.000483 | −0.005162 | −0.000495 | −0.000188 |
| $(\Delta E_{RR})_X$ | −0.000021 | 0.000325 | 0.000201 | 0.000043 |
| $\Delta E_{nuc}$ | 0.000001 | 0.000988 | 0.000067 | 0.000087 |
| $\Delta E_{L,1}$ | 0.009706 | 1.519836 | 0.101502 | 0.136100 |
| $\Delta E_{L,2}$ | −0.005930 | −0.140402 | −0.011022 | −0.001231 |
| Total | −6083.099414 | −198310.664244 | −32033.232106 | −38454.695136 |

Table 4
Contributions to the D-state energies ($\mathrm{cm}^{-1}$) from ref. [2]. The physical constants are as defined in table 3

| | $3\ {}^3D_3$ | $4\ {}^3D_1$ | $5\ {}^3D_1$ |
|---|---|---|---|
| $E_{NR}$ | −12209.084724 | −6866.166967 | −4393.505299 |
| $\Delta E_M^{(1)}$ | 0.000762 | 0.000886 | 0.000589 |
| $\Delta E_M^{(2)}$ | −0.000226 | −0.000127 | −0.000081 |
| $\Delta E_{rel}$ | −0.038056 | −0.001848 | −0.002654 |
| $(\Delta E_{RR})_M$ | −0.000034 | −0.000016 | −0.000009 |
| $(\Delta E_{RR})_X$ | 0.000020 | 0.000008 [a] | 0.000004 [a] |
| $\Delta E_{nuc}$ | 0.000000 | 0.000000 | 0.000000 |
| $\Delta E_{L,1}$ | −0.000372 | −0.000171 | −0.000090 |
| $\Delta E_{L,2}$ | −0.000082 | −0.000035 | −0.000018 |
| Total | −12209.122689 | −6866.168268 | −4393.507558 |

[a] Estimated from the $1/n^3$ scaling of the $3\ {}^3D$ value.

smaller than for the S states, a comparison with the experimental 1s2s ${}^3S_1$–1s$n$d ${}^3D$ transition frequencies of Hlousek et al. [1], the Giacobino and Biraben [26] can be interpreted as a measurement of the S state Lamb shift. As shown in table 5, there is an almost constant discrepancy of 0.00048(6) $\mathrm{cm}^{-1}$ between theory and experiment out of a total Lamb shift contribution of 0.13497 $\mathrm{cm}^{-1}$, such that the calculated 1s2s ${}^3S_1$ state lies too low by this amount. Considering the incomplete state of two-electron Lamb shift calculations, the agreement is remarkably good. For example, an upward shift of 0.00048 $\mathrm{cm}^{-1}$ is obtained if one reduces the magnitude of the Bethe logarithm screening parameter in eq. (22) from −0.01388 to −0.01306. Such a change could easily arise from higher order terms in the $1/Z$ expansion of the two-electron Bethe logarithm. If one attributes the entire discrepancy to the Bethe logarithm, then the experimental value of $\sigma$ for the 1s2s ${}^3S_1$ state is

Table 5
Comparison of experimental and theoretical $2\ {}^3S_1 - n\ {}^3D$ transition frequencies ($\mathrm{cm}^{-1}$)

| Transition | Theory | Experiment | Difference |
|---|---|---|---|
| $2\ {}^3S_1 - 3\ {}^3D_3$ | 26245.57245 | 26245.5719(5) [a] | 0.0005(5) |
| $2\ {}^3S_1 - 4\ {}^3D_1$ | 31588.52687 | 31588.52639(6) [b] | 0.00048(6) |
| $2\ {}^3S_1 - 5\ {}^3D_1$ | 34061.18758 | 34061.18709(8) [b] | 0.00049(8) |

[a] Giacobino and Biraben [26].
[b] Hlousek et al. [1].

$$\sigma_{exp} = -0.0131 \pm 0.0001.$$

If terms beyond $1/Z$ are negligible, then one obtains

$$\sigma = -0.01388 + Z^{-1} 0.0016(2).$$

Another possible source of the discrepancy is relativistic corrections of $O(\alpha^4)$ to the 1s2s ${}^3S_1$ state. However the leading two terms in the $1/Z$ expansion of this correction are known [27,28] and they indicate that there is a great deal of numerical cancellation. The result is

$$\Delta E_{rel}^{(4)}(1s2s\ {}^3S_1) = \left(-\tfrac{85}{1024} + \tfrac{1}{16}\right)\alpha^4 Z^6 + 0.04323\alpha^4 Z^5$$
$$= 0.000044 \quad \mathrm{cm}^{-1}$$

relative to $He^+(1s)$. This is too small by a factor of 10 to account for the discrepancy. A final resolution of the problem must await full two-electron relativistic and QED calculations.

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