# High Precision Calculation of Fine Structure Splittings in Helium and He-Like Ions

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Fine structure splittings for the $1s2p\,^3P$ state of helium are calculated to a computational accuracy of 3 parts in $10^9$, including all terms up to $O(\alpha^6 mc^2)$. The results differ notably from recent high precision measurements in He and $Be^{2+}$, but there is good agreement for $Li^+$, $B^{3+}$, and $F^{7+}$. A comparison with relativistic configuration interaction calculations [M H. Chen *et al.*, Phys. Rev. A **47**, 3692 (1993)] indicates close agreement for $Z \geq 10$, and lends strong support to both calculations.

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The theoretical calculation of fine structure splittings in the $1s2p\,^3P_J$ states of helium is a fundamental problem in atomic physics. Comparisons with high precision measurements [1–5] provide new tests of quantum electrodynamics (QED) in a system more complicated than hydrogen. The results will potentially yield a precise value for the fine structure constant $\alpha$ when all QED contributions are known to sufficient precision (see discussion at the end). We report here the first significant theoretical progress for helium since the early work of Douglas and Kroll [6], Hambro [7], Daley *et al.* [8], and Lewis and Serafino [9] for all terms up to $O(\alpha^6 mc^2)$, and the first extension of fully correlated variational calculations to heliumlike ions. The results complement, and eventually overlap, recent relativistic configuration interaction (CI) [10] and many body perturbation theory (MBPT) [11] calculations for high nuclear charge $Z$.

Our calculation begins with very accurate nonrelativistic variational wave functions constructed from double basis sets in Hylleraas coordinates, as described previously [12,13]. The spin-dependent level shift for a fine structure state with total angular momentum $J$ is then given by an expansion of the form (in atomic units)

$$\Delta E_J = \alpha^2\langle B_P\rangle_J + \alpha^4\langle B_P(E^0 - H^0)^{-1}B_P\rangle_J + \alpha^4\langle H_{\rm DK}\rangle_J + \cdots, \quad (1)$$

where $B_P$ is the reduced Breit interaction in two-component Pauli form (including anomalous magnetic moment corrections of relative order $\alpha/2\pi$) [14], the second term is the second-order correction due to $B_P$, and $H_{\rm DK}$ represents a sum of 16 spin-dependent operators derived by Douglas and Kroll [6] from the covariant Bethe-Salpeter equation. Recent work by Zhang and Drake [15,16] and by Eides, Khriplovich, and Milstein [17] has verified the partly phenomenological treatment of radiative corrections by Douglas and Kroll [6]. Although, in general, $B_P$ cannot be taken to second order, here we include only the positive frequency spin-dependent part, with the residual being accounted for by $H_{\rm DK}$.

The leading term of (1) must be known to the highest accuracy because it is multiplied by the lowest power of $\alpha \approx 1/137$. It accounts for the completely inverted fine structure of the helium $1s2p\,^3P_J$ state, with the $J = 0$ level lying highest. In previous work [12], the leading $\alpha^2\langle B_P\rangle_J$ term was calculated to an accuracy of better than 1 part in $10^9$, which is more than adequate for our purposes.

The next term $B_P^{(2)} = \alpha^4\langle B_P(E^0 - H^0)^{-1}B_P\rangle_J$ presents the greatest computational difficulties. The accuracy of this term limited the final accuracy claimed by Lewis and Serafino [9] for $\nu_{01}$ and $\nu_{12}$ to $\pm 0.043$ and $\pm 0.081$ MHz, respectively, although they considerably underestimated their uncertainties. Following the method of Dalgarno and Lewis [18], the calculation of $B_P^{(2)}$ can be cast in the form

$$B_P^{(2)} = \alpha^4\langle\Psi^{(1)}|B_P|\Psi^0\rangle, \quad (2)$$

where $\Psi^{(1)}$ satisfies the inhomogenous perturbation equation

$$(H^{(0)} - E^{(0)})\Psi^{(1)} + B_P\Psi^{(0)} = E^{(1)}\Psi^{(0)}, \quad (3)$$

and $\Psi^{(0)}$ is the unperturbed wave function expressed in terms of the doubled Hylleraas basis set. $\Psi^{(1)}$ is then expanded in terms of complete sets of $^3P^o$, $^1P^o$, $^3D^o$, $^1D^o$, and $^3F^o$ Hylleraas functions and Eq. (3) solved variationally. The problem is that the results are very slowly convergent with basis set size. This problem can be avoided by recognizing that terms such as the spin-orbit interaction are proportional to $1/r_2^3$, where $r_2$ is the radial coordinate of the $p$ electron, and the exact solutions to the corresponding hydrogenic perturbation equation are known to contain terms of the form $r^{-1}\Psi^{(0)}$ and $\ln r\Psi^{(0)}$ [19]. As shown in Fig. 1 for the second-order spin-orbit interaction, the rate of convergence is dramatically enhanced by augmenting the basis sets for $\Psi^{(1)}$ to include terms of the functional form $r_2^{-1}\Psi^{(0)}$ and $r_{12}^{-1}\Psi^{(0)}$, where $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$ is the interelectron coordinate. A further significant enhancement is obtained by including a few short range terms of the form

$$r_1^i r_2^j r_{12}^k \exp(-\alpha_S r_1 - \beta_S r_2)\cos\theta_2 \pm \text{exchange},$$

with $\alpha_S = \alpha_A$, $\beta_S = 25\beta_A$, and $\alpha_A, \beta_A$ are the corresponding nonlinear parameters in the asymptotic sector

  

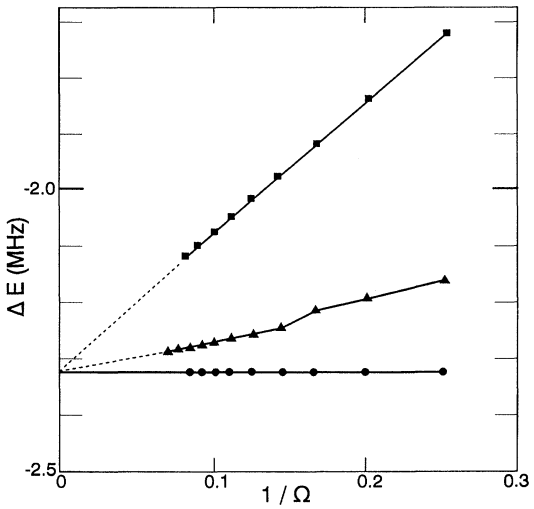


FIG. 1. Convergence of the second-order $^3P^o$ spin-orbit interaction with basis set size defined by $\Omega = (i + j + k)_{\max}$. Top curve, results of Lewis and Serafino [9]; middle curve, double basis set; bottom curve, augmented basis set (see text). The extrapolated value at $1/\Omega = 0$ is $\Delta E = -2.320\,721(4)$ MHz.

$A$ of the doubled basis set for $\Psi^{(0)}$. Their values are $\alpha_A = 2a_0^{-1}$ and $\beta_A \approx 1a_0^{-1}$. The large value for $\beta_S$ makes these terms significant only for small $r_2$. The final augmented basis sets contain up to 1890 terms. Table I shows a comparison with the results of Lewis and Serafino for the contributions of $B_P^{(2)}$ to the $\nu_{12}$ interval of helium. The contributions from the dominant $^3P^o$ and $^1P^o$ intermediate states were their main source of uncertainty. For these, the accuracy is now improved by about 3 orders of magnitude to $\pm 0.07$ kHz. The small $^3F^o$ contribution remains somewhat slowly convergent and is now the dominant source of uncertainty for $\nu_{12}$. However, the $^3F^o$ states do not contribute to $\nu_{01}$, and so the final accuracy is correspondingly better.

The final step in the calculation is the evaluation of the $\langle H_{\rm DK}\rangle_J$ term in Eq. (1). We have previously presented a general procedure for canceling the singularities that occur and evaluating the finite residual part in Hylleraas coordinates [20]. The result obtained with wave functions containing up to 804 terms [12,13] without finite mass corrections is $-3.335\,188(13)$ MHz for $\nu_{01}$ and $1.533\,930(21)$ MHz for $\nu_{12}$. These values are much more accurate than the older values $-3.331(4)$ and $1.542(7)$ MHz obtained by Daley *et al.* [8].

TABLE I. Comparison of second-order Breit contributions of $O(\alpha^4)$ a.u. to $\nu_{12}$ with the results of Lewis and Serafino [9]. Units are $\alpha^4 {\rm Ry} = 9.329\,029\,7$ MHz.

| Intermediate states | Present work | Lewis and Serafino | Difference |
|---|---|---|---|
| $^3P^o$ | −0.168 255(7) | −0.155(8) | −0.013(8) |
| $^1P^o$ | −0.707 003(1) | −0.704 1(20) | −0.002 9(20) |
| $^3D^o$ | 0.005 413(0) | 0.005 19(21) | 0.000 22(21) |
| $^1D^o$ | 0.002 380(0) | 0.002 378(1) | 0.000 002(1) |
| $^3F^o$ | 0.005 61(4) | 0.004 8(8) | 0.000 8(8) |
| Total | −0.861 85(4) | −0.847(8) | −0.014(8) |

The remaining terms to be taken into account arise from finite nuclear mass and mass polarization effects. The corrections are of order $\mu/M$ and $(\mu/M)^2$ relative to the leading terms displayed in Eq. (1), where $\mu = mM/(m + M)$ is the reduced electron mass, and $M$ is the nuclear mass. The mass scaling of each term gives a contribution, together with the Stone [21] term which arises from the transformation of the Breit interaction to center-of-mass coordinates. All these terms have been discussed in detail previously [12,13,22]. We obtained the remaining mass polarization correction by including the mass polarization operator $(\mu/M)\mathbf{p}_1 \cdot \mathbf{p}_2$ explicitly in the nonrelativistic Hamiltonian and repeating each calculation to find the mass dependent shift. This procedure sums to infinity the $\alpha^2\mu/M$ perturbation terms calculated by Lewis and Serafino [9]. In Table II, the small finite mass correction labeled as $(\mu/M)^2\alpha^2$, in fact, contains all higher powers of $\mu/M$.

Table II displays the final results for the fine structure splittings of helium. Higher order terms in $\alpha Z$ must still be considered, but to the extent that they can be neglected, the indicated accuracy for $\nu_{01}$ is $\pm 0.1$ kHz, or 3 parts in $10^9$. The predicted splittings are in reasonable agreement with the older measurements of Hughes and co-workers [23], but differ markedly from the recent $\pm 3$ kHz measurements of Shiner and co-workers [1]. Although $\nu_{12}$ is

TABLE II. Contributions to the theoretical fine structure intervals for the $1s2p\ ^3P_J$ states of helium and comparison with experiment. Units are MHz, using $R_\infty = 3\,289\,841\,961.07(54)$ MHz, $\alpha^{-1} = 137.035\,989\,5(61)$, and $\mu/M = 1.370\,745\,620(30) \times 10^{-4}$.

| Term | $\nu_{01}$ | $\nu_{12}$ |
|---|---|---|
| $\alpha^2$ | 29.564.600 020(5)[a] | 2 317.232 220(5) |
| $\alpha^2$ | 29 564.577(6)[b] | 2 317.203(1)[b] |
| $\alpha^2\mu/M$ | −0.830 968 | 3.009 638 |
| $\alpha^2(\mu/M)^2$ | 0.000 800(5) | −0.000 082(5) |
| $\alpha^3$ | 54.707 868 | −22.548 217 |
| $\alpha^3\mu/M$ | −0.003 820 | 0.003 215 |
| $\alpha^4$ | −1.607 7(1) | −6.506 4(3) |
| $\nu_{\rm total}$ | 29 616.866 2(1) | 2 291.190 4(3) |
| $\nu_{\rm exp}$ I[c] | 29 616.844(21) | 2 291.196(5) |
| $\nu_{\rm exp}$ II[d] | 29 616.962(3) | 2 291.174(3) |
| $\nu_{\rm total} - \nu_{\rm exp}$ I | 0.022(21) | −0.006(5) |
| $\nu_{\rm total} - \nu_{\rm exp}$ II | −0.096(3) | 0.016(3) |

[a]Numbers in brackets are computational uncertainties. Uncertainties due to higher order terms not calculated are ~60 kHz (see text).
[b]Lewis and Serafino, Ref. [9].
[c]Hughes *et al.*, Ref. [23].
[d]Shiner *et al.*, Ref. [1].

TABLE III. Comparison of theoretical and experimental fine structure intervals for the $1s2p\ ^3P_J$ states of $Li^+$, $Be^{2+}$, $B^{3+}$, and $F^{7+}$. Units are MHz for $Li^+$ and $cm^{-1}$ for the others.

| Interval | Present work | CI[a] | Experiment |
|---|---|---|---|
| | $Li^+$ | | |
| $\nu_{01}$ | 155 704.216 1(30) | | 155 704.27(66)[b] |
| $\nu_{12}$ | −62 678.338 2(27) | | −62 678.41(66)[b] |
| | $Be^{2+}$ | | |
| $\nu_{01}$ | 11.557 660 5(7) | | 11.558 6(5)[c] |
| $\nu_{12}$ | −14.892 209(1) | | −14.895 0(4)[c] |
| | $B^{3+}$ | | |
| $\nu_{01}$ | 16.197 573(2) | 16.20(3) | 16.203(18)[d] |
| $\nu_{12}$ | −52.661 199(4) | −52.65 | −52.660(16)[d] |
| | $F^{7+}$ | | |
| $\nu_{01}$ | −151.246 6(1) | −151.24 | |
| $\nu_{12}$ | −957.848 7(2) | −957.85 | −957.883(19)[e] |

[a]Chen *et al.*, Ref. [10].
[b]Riis *et al.*, Ref. [2].
[c]Scholl *et al.*, Ref. [3].
[d]Dinneen *et al.*, Ref. [4].
[e]Myers *et al.*, Ref. [5].

in reasonably good agreement, the difference for $\nu_{01}$ is 96(3) kHz.

In view of this large discrepancy, it is important to find ways of checking the accuracy of the calculations and possible contributions from higher order terms not included. One check is provided by the comparison in Table III for fine structure splittings in ions from $Li^+$ to $F^{7+}$. Except for $Be^{2+}$, where there are significant discrepancies, theory and experiment are in good agreement. Although the measurements are less accurate than for helium, the leading term not included is known from the spin-dependent part of the one-electron Lamb shift to be

$$\Delta E_j = \frac{\alpha^5 Z^6}{3\pi n^3}\left(1 - \frac{1}{n^2}\right)\ln(Z\alpha)^{-2}\delta_{j,1/2}\delta_{L,1}, \qquad (4)$$

and so increases rapidly with $Z$. After replacing the factor of $Z^6$ by $Z(Z-1)^5$ to allow for screening, and converting to $LS$ coupling, $\Delta E_j$ increases $\nu_{12}$ by 15 kHz, 662 kHz, and 0.048 $cm^{-1}$, respectively, for He, $Li^+$, and $F^{7+}$. The increases are half as big for $\nu_{01}$. For $Li^+$ and $F^{7+}$, the additional shift is about the size of the experimental uncertainty, but the corresponding change to $\nu_{01}$ for He is much too small to account for the discrepancy. There may be unexpectedly large two-electron corrections for low $Z$, but it is probably not unreasonable to take the uncertainty due to uncalculated terms as ±60 kHz for helium.

A second check is provided by a comparison with the relativistic CI calculations of Chen, Cheng, and Johnson (CCJ) [10], which achieve sufficient accuracy for this purpose for $Z \geq 10$. We compare terms in the $Z^{-1}$ expansion of $\alpha^4[B_P^{(2)} + \langle H_{\rm DK}\rangle]$ with the corresponding terms identified by CCJ. Since the leading two terms are known from one-electron Dirac theory [24,25], the non-QED part of the $\alpha^4$ contribution to $\nu_{02}$ assumes the form

$$\nu_{02}^{(4)} = (Z\alpha)^4[-\tfrac{5}{256}Z^2 + 0.144\,772\,9Z + c_{02} + \cdots],$$

where $c_{02}$ is the leading coefficient to be determined. A fit to our numerical results in the range $Z = 2$ to 12 yields $c_{02} = -0.464\,5(20)$, which is consistent with the value −0.51 quoted by CCJ. For the 1–2 interval, the $2^1P_1$-$2^3P_1$ contribution to singlet-triplet mixing must first be subtracted from the $2^3P_1$ state energy to obtain the remaining shift

$$\nu_{12}^{\prime(4)} = (Z\alpha)^4[-\tfrac{5}{384}Z^2 + 0.058\,776\,8Z - 0.13(1) + \cdots],$$

in comparison with −0.154 obtained by CCJ for the final coefficient. The agreement in these coefficients provides strong support for both sets of calculations in the range of moderately large $Z$. The comparison between the present work and the CI calculations in Table III shows that the total splittings come into progressively close agreement with increasing $Z$ [26]. The MBPT calculations of Ref. [11] are essentially the same. The addition of the above corrections of $O(Z^4\alpha^4)$ to the "unified method" [27] would also bring those results into agreement.

Since $\nu_{01}$ is ~29 617 MHz and is proportional to $\alpha^2$ in lowest order, a comparison between theory and experiment at the ±1 kHz level would determine $\alpha$ to a precision of 16 ppb (parts per billion). Currently, the best measurements from the ac Josephson and quantum Hall effects are [28]

$$\alpha^{-1}(\text{acJ}) = 137.035\,977\,0(77)\ (56\ \text{ppb}),$$

$$\alpha^{-1}(\text{QHE}) = 137.035\,997\,9(32)\ (24\ \text{ppb}).$$

These differ from each other by 153 ppb, and from the $g-2$ value

$$\alpha^{-1}(g-2) = 137.035\,992\,22(94)\ (6.9\ \text{ppb})$$

by 111 and 41 ppb, respectively. A new atomic physics determination from $\nu_{01}$ at the ±1 kHz level would be more than sufficient to distinguish among these determinations. Unlike the $g-2$ measurement, the fine structure splittings are to lowest order a non-QED effect, and are therefore less sensitive to high-order QED corrections by a factor of $\alpha^{-1}$.

Completion of the theory to better than ±1 kHz will require the calculation of spin-dependent corrections of order $\alpha^4\mu/M$, $\alpha^5\ln\alpha$, and $\alpha^5$. The first is relatively straightforward, but the latter two will require the extension of known atomic theory to the next higher power in $\alpha$. Work on this problem is in progress [29]. Once this is completed, the residual uncertainty due to terms of $O(\alpha^6)$ and smaller will be ~0.5 kHz.

In summary, we have greatly improved the accuracy of fine structure calculations for helium, and obtained results comparable to experimental accuracies for He-like ions up to $F^{7+}$. There is good agreement for $Li^+$, $B^{3+}$, and $F^{7+}$, but notable discrepancies for He and $Be^{2+}$.

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