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Fine structure for *D* and *F* states of the helium isoelectronic sequence*

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A systematic study is made of the *D*- and *F*-state fine structure of the helium isoelectronic sequence with particular regard to its *n* and *Z* dependence. Our theoretical results are compared with available experiments as well as with other theoretical calculations.

I. INTRODUCTION

High-precision measurements of the fine structure of the singly excited He(1s, nl) spectra of higher angular momentum states ($L \geq 2$) have become available in recent years. In a microwave-optical resonance measurement, Wing, Lamb, and their co-workers[1,2] have obtained the electrostatic fine-structure level splitting of singly excited F states as well as the transition frequencies between D and F states. In a level-crossing measurement, Descoubes[3] measured the fine structure of $n\,^3D$ states up to $n = 7$. The same spectra have also been obtained by Berry *et al.*[4] using the beam-foil technique. More recently, using the method of level anticrossing, Miller *et al.*[5] have measured "directly" the singlet-triplet level splittings of nD states. These high-precision experiments yield results several orders of magnitude better than the previous measurements of optical transitions and have opened a new horizon on the detailed study of atomic Rydberg states.

The physics of high Rydberg states holds special intrinsic interest not only because of its quasihydrogenic nature but also because of its close relation to the scattering of slow electrons by the charged ion core. The applications of these studies also include radioastronomy, laser-induced-isotope separation, as well as the determination of fundamental constants to improved accuracy.

On the theoretical side, earlier works on the electrostatic fine structure of higher angular momentum states ($L \geq 2$) relied mostly on the well-known polarization model,[6] which has also been employed extensively by atomic spectroscopists. Recently, more elaborate calculations have been carried out[7-9] with a large number of correlated Hylleraas-type basis sets, similar to those used by Accad *et al.*[10] in their extensive calculations of the fine structures of S and P states. However, in these variational calculations the desired numerical accuracy becomes increasingly difficult to achieve as n and l increase. Furthermore, as the degree of excitation increases, the pure singlet-triplet description becomes unrealistic when the spin-orbit interactions become comparable to the exchange interaction. The general formulation of the fine structure of the two-electron system with spin-dependent interaction included, as developed by Araki[11] and recently extended by Parish and Mires,[12] must be used. However, the numerical calculation of Parish and Mires fails to predict quantitatively the fine-structure level splittings of D and F states obtained in the experimental measurement mentioned above.

Recently we have carried out a more complete theoretical study of the helium Rydberg states using a perturbation-theory approach.[13] It was found that the contribution from the second-order exchange interaction is much too large to be ignored. By including this second-order exchange interaction and employing the method of Araki, we have brought the singlet-triplet level splittings of D and F states, as well as the transition frequency between D and F states, into excellent agreement with the experimental results in the case of helium. This positive result encourages us to extend our calculation to other atomic Rydberg states, particularly those of the helium isoelectronic series. In this paper, we report the result of such an extension on the fine structure of D and F states for two-electron atomic systems up to $Z = 10$.

It is perhaps worth mentioning at this point two distinct advantages of the perturbation approach. First, a physical interpretation of the contributing terms in the perturbation series gives a much better understanding of the physical processes. Second and more relevant here is the high accuracy the perturbation-theory approach is able to yield. This stems from the fact that in a perturbation approach, one often reduces the calculation to the direct evaluation of the terms of interest. Thus, one may maintain the same level of high accuracy for different physical quantities, such as level splittings and level shifts, whose value may differ by many orders of magnitude. In contrast, the variational-theory approach calculates the physical quantities of interest such as level-splitting by taking the difference of two nearly equal quantities. The numerical accuracy of the result can become rather poor even after an elaborate calculation.

One should also point out here that another physical effect, the hyperfine interactions, may also contribute to the level splittings. However, while both electrostatic and spin-orbit fine structures have rather smooth and systematic dependence on Z and n, the hyperfine structure varies according to the nuclear spin I and nuclear g factor. It is therefore necessary to treat the hyperfine structure on a case-to-case base. We have restricted our present calculation to the electrostatic and spin-orbit interactions.

In Sec. II, we review the calculational procedures and discuss the Z and n dependence of the physical quantities of interest, and we obtain the general parameters from numerically calculated points by appropriate interpolation and extrapolation procedures. Finally, in Sec. III, we present the results of our calculation in a number of Tables. In Tables I–VI, we compare our results with available experiments. Tables VII–X present the fitted parameters. In Tables XI–XIII we present comparisons with other previous theoretical results. Discussions and conclusions are also presented.

II. CALCULATIONAL PROCEDURES

Starting from two unperturbed hydrogenic electron orbitals (one with charge Z, the other $Z-1$), the energy value of a given level $n\,{}^{2S+1}L_J$ for a two-electron system with one electron in the 1s orbit and the other in an nl orbit is given in Ry units by

$$E({}^{2S+1}L_J;n,Z) = -[Z^2+(Z-1)^2/n^2]+\Delta E_d(L;n,Z) + \Delta E_{fs}({}^{2S+1}L_J;n,Z), \tag{1}$$

where Z indicates the nuclear charge. The detailed perturbation treatment of the direct interaction ΔE_d was given in Ref. 13. The general treatment of the level splitting ΔE_{fs}, as we mentioned in Sec. I, was developed by Araki[11] and later extended by Parish and Mires.[12] In the present calculation, the exchange interaction term K which appears in Araki's formalism is obtained in the more complete perturbation treatment up to and including the second-order exchange effect as described in Ref. 13.

To minimize the computational effort and to take advantage of the fact that $E({}^{2S+1}L_J;n,Z)$ varies smoothly with n and Z, one of our major tasks is to find the appropriate expansion parameters which represent the level positions of the *entire* Rydberg series. That is, we first calculate numerically ΔE_d and ΔE_{fs} at a sufficient number of n and Z for given L, using the procedure described in a previous paragraph. We then use a least-squares-fit procedure to obtain those parameters which, in turn, will generate the level positions of the *entire* Rydberg series for given Z and L.

We now proceed to discuss the parametrization procedures for the calculations of ΔE_d and ΔE_{fs}. First let us consider the n dependence. For given L and Z, it has been shown[6] that both ΔE_d and ΔE_{fs} for large n states are proportional to n^{-3}, while for smaller n states, additional n-dependent terms should also be included. The appropriate n dependence is then[6,14]

$$\frac{a}{n^3}+\frac{b}{n^5}+\frac{c}{n^7}+\cdots . \tag{2}$$

This n dependence has been verified in recent experimental[2] and theoretical[13,14] investigations of the fine structure of Rydberg states of the helium atom. It has also been utilized[14] in removing an unexpected n^{-2} dependence of the fine-structure level splitting of Be IV and C V. In the present calculation, we have included the first three terms of Eq. (2) for both D and F Rydberg series, i.e., setting

$$\Delta E_d(L;n,Z)=\frac{A(L,Z)}{n^3}+\frac{B(L,Z)}{n^5}+\frac{C(L,Z)}{n^7}, \tag{3}$$

$$\Delta E_{fs}({}^{2S+1}L_J;n,Z)=\frac{a({}^{2S+1}L_J,Z)}{n^3}+\frac{b({}^{2S+1}L_J,Z)}{n^5} +\frac{c({}^{2S+1}L_J,Z)}{n^7}. \tag{4}$$

Next, let us consider the Z dependence. The Z dependence of ΔE_{fs} is less apparent when Araki's method is employed. Nevertheless, the Z dependence of all the dominant parameters (i.e., λ, ζ, and η in Ref. 12) associated with the spin-dependent interactions for higher angular momentum states is given analytically. Thus, we shall only focus our attention on the Z dependence of the electrostatic exchange interaction K for given n and L. For large n, the Z dependence of K is approximately given by[15]

$$Z\left(\frac{Z-1}{Z}\right)^{2l+3}\exp\left(\frac{-2(Z-1)}{Z}\right). \tag{5}$$

For large Z, this can be expanded as

TABLE I. Comparison between the results of the present calculation and high-precision experimental measurements of singlet-triplet level splittings ($^1L_{J=L} - {}^3L_{J=L}$) of He I (in unit of GHz).

	Experiments				
(1*s*,*nl*)	Wing *et al.*[a]	Miller *et al.*[b]	BK[c]	Derouard *et al.*[d]	Present theory
(1*s*, 6*f*)	$(226.64 \pm 0.11) \times 10^{-3}$	...	...	...	222.5×10^{-3}
(1*s*, 7*f*)	$(146.3 \pm 0.2) \times 10^{-3}$	...	...	...	143.1×10^{-3}
(1*s*, 10*f*)	51.30×10^{-3}	...	...	...	50.76×10^{-3}
(1*s*, 11*f*)	39.50×10^{-3}	...	...	...	38.36×10^{-3}
(1*s*, 3*d*)	...	...	...	102.36 ± 0.2	102.0
(1*s*, 4*d*)	...	...	...	59.14 ± 0.08	58.86
(1*s*, 5*d*)	...	...	...	34.125 ± 0.045	33.92
(1*s*, 6*d*)	20.9338	20.906 ± 0.02	...	20.946 ± 0.03	20.82
(1*s*, 7*d*)	13.6487	13.625 ± 0.03	...	13.646 ± 0.03	13.57
(1*s*, 8*d*)	...	9.47 ± 0.035	9.326 ± 0.035	9.365 ± 0.035	9.29
(1*s*, 9*d*)	...	...	6.644 ± 0.035	...	6.62
(1*s*, 10*d*)	...	...	4.889 ± 0.030	...	4.87
(1*s*, 11*d*)	...	...	3.696 ± 0.030	...	3.69

[a] Wing *et al.* (Ref. 1 and 2).
[b] Miller *et al.* (Ref. 5).
[c] Beyer and Kollath (Ref. 18).
[d] Derouard *et al.* (Ref. 17).

$$aZ + b + \frac{c}{Z} + \frac{d}{Z^2} + \cdots . \tag{6}$$

Furthermore, the second-order exchange interaction in the perturbation series can be expanded as

$$\left(a'Z + b' + \frac{c'}{Z} + \frac{d'}{Z^2} + \cdots\right)^2 \Big/ Z^2 .$$

or

$$a'' + \frac{b''}{Z} + \frac{c''}{Z^2} + \cdots . \tag{7}$$

However, a better parametrization procedure is the following. As remarked in our previous paper, the ratio R between the second-order and first-order exchange interactions depends on L only for a given Z. Also, the value of R varies slowly as Z increases. Since the first-order electrostatic exchange can be calculated either analytically or numerically with very high accuracy, we find that it is advantageous to parametrize the Z dependence of R,

$$R = \frac{A}{Z} + \frac{B}{Z^2} + \frac{C}{Z^3} , \tag{8}$$

TABLE II. Comparison between the results of the present calculation and available spectroscopic data for the ^3D_J fine structures of He I (in $10^{-2}\,\mathrm{cm}^{-1}$).

		Experiments			Theories	
n	*J*-*J'*	BSC[a]	D[b]	Others	PM[e]	Present
3	1-2	4.500 ± 0.083	...	4.533 ± 0.1[c]	4.50	4.41
	2-3	0.237 ± 0.007	0.242 ± 0.002		0.43	0.232
4	1-2	1.788 ± 0.1	...	1.871 ± 0.1[c]	1.91	1.85
	2-3	0.133 ± 0.017	0.119 ± 0.0013	...	0.20	0.105
5	1-2	0.967 ± 0.067	0.943 ± 0.02	...	0.98	0.947
	2-3	0.063 ± 0.01	0.068 ± 0.001	...	0.11	0.055
6	1-2	0.500 ± 0.067	0.526 ± 0.1	0.553[d]	0.57	0.547
	2-3	...	0.041 ± 0.001	0.041[d]	0.066	0.032
7	1-2	0.303 ± 0.049	...	0.3199[d]	0.36	0.344
	2-3	...	0.024 ± 0.001	0.0237[d]	0.042	0.021

[a] Berry *et al*. (Ref. 4).
[b] Descoubes (Ref. 3).
[c] Brochard *et al.* (Ref. 20).
[d] MacAdam and Wing (Ref. 2).
[e] Parish and Mires (Ref. 12).

TABLE III. Comparison between the results of the present calculation and experimental data for singlet-triplet level splittings of Li II (in cm^{-1}).

n	Theory ($^1D_2$-$^3D_2$)	Expt. ($^1D_2$-$^3D_{av}$)[a]	Theory – Expt.
3	30.3	29.76	0.54
4	17.1	17.27	−0.22
5	9.72	10.07	−0.35
6	5.93	6.32	−0.39
7	3.85	4.30	−0.45
8	2.63	3.03	−0.40

[a] Herzberg and Moore (Ref. 21).

and thus obtain the second-order exchange interaction through R and hence the value of ΔE_{fs}. Now, the Z dependence of ΔE_d for given L and n is given by[16]

$$E_1(n,L)Z + E_2(n,L) + E_3(n,L)/Z + \cdots . \tag{9}$$

This Z-dependent series has been employed recently by Blanchard and Drake[7] in their calculation of energies of $1s3d(^{1,3}D)$ and $1s4d(^{1,3}D)$ states of the helium isoelectronic sequence for $Z = 2$–10.

Finally, we summarize the details of our calculational procedures as follows:

(a) We evaluate the direct level shift $\Delta E_d(L;n,Z)$ and the electrostatic exchange energy up to second order for D and F states of $Z = 2, 3, 5, 8$ and $n = 5, 7, 9, 11$.

(b) We proceed to fit the ratio $R(Z)$ with Eq. (8).

(c) We evaluate the first-order exchange for $Z = 4, 6, 7, 9, 10$ and $n = 5, 7, 9, 11$.

(d) By employing the fitted Eq. (8), we obtain the exchange energy K up to second order for $Z = 2$–10, $n = 5, 7, 9, 11$, and $L = 2, 3$.

(e) We evaluate the level splitting of D and F states for $n = 5, 7, 9, 11$ and $Z = 2$–10.

(f) We obtain $E_1(n,L)$, $E_2(n,L)$, and $E_3(n,L)$ for $n = 5, 7, 9, 11$ and $L = 2, 3$ by employing the fitted Eq. (9) and then in turn we evaluate $\Delta E_d(L;n,Z)$ for $Z = 2$–10, $n = 5, 7, 9, 11$, and $L = 2, 3$.

(g) We fit the appropriate level shifts and level splittings to obtain the general parameters in Eqs. (3) and (4).

III. RESULTS AND DISCUSSIONS

The results obtained in this calculation are presented in three groups of tables. The first group, from Tables I–VI, are the selections of our results where a comparison with experimental results is available. Table I gives the results of the present calculation and the recent high-precision experimental measurements of singlet-triplet level splittings ($^1L_{J=L} - {}^3L_{J=L}$) of He I. The availability of four sets of experimental data amply demonstrates the current activity in the experimental study of the neutral-helium Rydberg states; the exceedingly good agreement of our result with experiment throughout the available data is indeed gratifying. In this comparison we have not listed the time-honored results from optical data,[19] which, while extensive, have definitely been superseded in accuracy by this new generation of experiments.

Comparison between the results of the present

TABLE IV. Comparison between the results of the present calculation and experimental data for singlet-triplet level splittings of Be III (in cm^{-1}).

		Experiment ($^1D_2$-$^3D_{av}$)	
n	Theory ($^1D_2$-$^3D_2$)	Eidelsberg[a]	Löfstrand[b]
3	82.6	81.5 ± 6	79 ± 4
4	45.8	49.3 ± 4	44 ± 6
5	25.9	36.0 ± 14	(25)[c]
6	15.8		(16)
7	10.2		(10)
8	6.97		(7)

[a] Eidelsberg (Ref. 22).

[b] Löfstrand (Ref. 23).

[c] Values in parentheses are given by Ritz formula (Ref. 6).

TABLE V. Comparison between the results of the present calculation and the experimental data for singlet-triplet level splittings of B IV (in cm^{-1}).

n	Theory ($^1D_2$-$^3D_2$)	Expt. ($^1D_2$-$^3D_{av}$)[a]
3	153	144 ± 8
4	83.7	82 ± 43
5	47.2	(48)[b]
6	28.6	(30)
7	18.5	(19)
8	12.6	(12)

[a] Eidelsberg (Ref. 24).

[b] Values in parentheses are given by Ritz formula (Ref. 6).

TABLE VI. Comparison between the results of the present calculation and the experimental data for singlet-triplet level splittings of C v (in cm^{-1}).

n	Theory ($^1D_2$-$^3D_2$)	Expt. ($^1D_2$-$^3D_{\mathrm{av}}$) [a]
3	236	219 ± 16
4	128	147 ± 33
5	72.0	
6	43.6	

[a] Edlén and Löfstrand (Ref. 25).

calculation and the available experimental data for the ^3D_J fine structures of He I is presented in Table II. Here the uncertainties of the experimental results are much larger, as are the discrepancies between different experiments. Our theoretical result again gives good agreement throughout. We have also presented the theoretical results of Parish and Mires,[12] which give poorer agreement with experiment because of their inadequate account of the dynamic exchange interaction. In the J-J' = 2-3 cases their result is almost a factor of 2 too large.

Experimental data on the two-electron Rydberg states for nuclear charge $Z \geq 3$ are still rather meager, owing undoubtedly to the lack of adequate ion sources and other experimental difficulties. The presence of hyperfine interaction further complicates the situation, and different spin-coupling schemes may be necessary.[21] In Table III we

TABLE VII. Fitted parameters A, B, and C (in 10^{-2} Ry) for ΔE_d direct as given in Eq. (3). Numbers in parentheses indicate the powers of 10 by which the entries are to be multiplied.

L	Z	$A(Z,L)$	$B(Z,L)$	$C(Z,L)$
2	2	−4.934 (−1)	1.058	−6.553 (−1)
	3	−1.614	3.630	−2.076
	4	−2.778	6.733	−5.324
	5	−3.861	9.717	−5.139
	6	−4.876	1.255 (+1)	−2.070
	7	−5.842	1.526 (+1)	3.080
	8	−6.773	1.788 (+1)	9.722
	9	−7.679	2.042 (+1)	1.745 (+1)
	10	−8.565	2.292 (+1)	2.600 (+1)
3	2	−8.800 (−2)	5.037 (−1)	−1.652
	3	−2.774 (−1)	1.610	−5.506
	4	−4.498 (−1)	2.721	−1.050 (+1)
	5	−5.857 (−1)	3.549	−1.284 (+1)
	6	−6.953 (−1)	4.157	−1.298 (+1)
	7	−7.867 (−1)	4.610	−1.154 (+1)
	8	−8.655 (−1)	4.955	−8.986
	9	−9.353 (−1)	5.220	−5.614
	10	−9.983 (−1)	5.427	−1.636

TABLE VIII. Fitted parameters a, b, and c (in 10^{-1} Ry) for ΔE_{fs} of $^1D_2$ and $^1F_3$ states as given in Eq. (4). Numbers in parentheses indicate the powers of 10 by which the entries are to be multiplied.

$^{2S+1}L_J$	Z	$a(Z, {}^{2S+1}L_J)$	$b(Z, {}^{2S+1}L_J)$	$c(Z, {}^{2S+1}L_J)$
$^1D_2$	2	7.722 (−3)	−3.234 (−2)	3.998 (−3)
	3	6.503 (−2)	−2.419 (−1)	−8.228 (−2)
	4	1.712 (−1)	−5.918 (−1)	−3.672 (−1)
	5	3.085 (−1)	−1.017	−8.034 (−1)
	6	4.658 (−1)	−1.482	−1.336
	7	6.373 (−1)	−1.969	−1.912
	8	8.209 (−1)	−2.463	−2.679
	9	1.017	−2.951	−3.000
	10	1.229	−3.419	−3.426
$^1F_3$	2	7.675 (−5)	−2.951 (−4)	1.685 (−3)
	3	1.031 (−3)	−7.414 (−3)	3.884 (−2)
	4	3.994 (−3)	−2.462 (−2)	1.276 (−1)
	5	1.001 (−2)	−4.499 (−2)	2.368 (−1)
	6	2.067 (−2)	−6.278 (−2)	3.302 (−1)
	7	3.825 (−2)	−7.638 (−2)	3.929 (−1)
	8	6.554 (−2)	−8.657 (−2)	4.282 (−1)
	9	1.058 (−1)	−9.458 (−2)	4.445 (−1)
	10	1.628 (−1)	−1.014 (−1)	4.495 (−1)

TABLE IX. Fitted parameters a, b, and c (in 10^{-1} Ry) for ΔE_{fs} of ^3D_J states as given in Eq. (4). Numbers in parentheses indicate the powers of 10 by which the entries are to be multiplied.

$^{2S+1}L_J$	Z	$a(Z, {}^{2S+1}L_J)$	$b(Z, {}^{2S+1}L_J)$	$c(Z, {}^{2S+1}L_J)$
$^3D_1$	2	−7.632 (−3)	3.235 (−2)	−3.971 (−3)
	3	−6.473 (−2)	2.419 (−1)	8.255 (−2)
	4	−1.716 (−1)	5.921 (−1)	3.691 (−1)
	5	−3.126 (−1)	1.018	8.115 (−1)
	6	−4.798 (−1)	1.487	1.363
	7	−6.713 (−1)	1.982	1.984
	8	−8.893 (−1)	2.494	2.646
	9	−1.139	3.017	3.349
	10	−1.427	3.549	4.084
$^3D_2$	2	−7.740 (−3)	3.234 (−2)	−3.999 (−3)
	3	−6.531 (−2)	2.419 (−1)	8.231 (−2)
	4	−1.726 (−1)	5.918 (−1)	3.673 (−1)
	5	−3.130 (−1)	1.017	8.036 (−1)
	6	−4.769 (−1)	1.482	1.337
	7	−6.603 (−1)	1.969	1.913
	8	−8.635 (−1)	2.463	2.479
	9	−1.090	2.951	3.000
	10	−1.346	3.419	3.426
$^3D_3$	2	−7.746 (−3)	3.235 (−2)	−3.974 (−3)
	3	−6.493 (−2)	2.419 (−1)	8.257 (−2)
	4	−1.699 (−1)	5.921 (−1)	3.690 (−1)
	5	−3.028 (−1)	1.018	8.111 (−1)
	6	−4.497 (−1)	1.487	1.362
	7	−6.001 (−1)	1.982	1.983
	8	−7.458 (−1)	2.494	2.645
	9	−8.791 (−1)	3.017	3.348
	10	−9.924	3.549	4.084

TABLE X. Fitted parameters a, b, and c (in 10^{-2} Ry) for ΔE_{fs} of ^3F_J states as given in Eq. (4). Numbers in parentheses indicate the powers of 10 by which the entries are to be multiplied.

$^{2S+1}L_J$	Z	$a(Z, {}^{2S+1}L_J)$	$b(Z, {}^{2S+1}L_J)$	$c(Z, {}^{2S+1}L_J)$
$^3F_2$	2	−6.526 (−5)	5.114 (−3)	−7.148 (−3)
	3	−6.905 (−3)	9.728 (−2)	−2.518 (−1)
	4	−3.201 (−2)	3.433 (−1)	−8.187 (−1)
	5	−8.565 (−2)	7.215 (−1)	−1.596
	6	−1.826 (−1)	1.197	−2.502
	7	−3.443 (−1)	1.741	−3.487
	8	−5.989 (−1)	2.337	−4.531
	9	−9.810 (−1)	2.970	−5.613
	10	−1.532	3.631	−6.724
$^3F_3$	2	−8.309 (−4)	2.951 (−3)	−1.685 (−2)
	3	−1.132 (−2)	7.414 (−2)	−3.884 (−1)
	4	−4.508 (−2)	2.462 (−1)	−1.276
	5	−1.163 (−1)	4.499 (−1)	−2.368
	6	−2.463 (−1)	6.278 (−1)	−3.302
	7	−4.646 (−1)	7.638 (−1)	−3.629
	8	−8.075 (−1)	8.657 (−1)	−4.282
	9	−1.318	9.458 (−1)	−4.445
	10	−2.044	1.014	−4.494
$^3F_4$	2	−5.690 (−4)	5.251 (−3)	−1.066 (−2)
	3	−7.378 (−3)	9.728 (−2)	−2.518 (−1)
	4	−2.162 (−2)	3.433 (−1)	−8.186 (−1)
	5	−3.264 (−2)	7.216 (−1)	−1.597
	6	−2.363 (−2)	1.198	−2.520
	7	2.631 (−2)	1.740	−3.464
	8	1.419 (−1)	2.336	−4.517
	9	3.519 (−1)	2.969	−5.602
	10	6.895 (−1)	3.631	−6.716

present the comparison of our calculation with the experiment of Herzberg and Moore[21] for the singlet-triplet level splittings of Li II. While the agreement is reasonable, it is interesting to note that the difference between our theory and the experiment seems to reach a constant value as n becomes large. This suggest that the difference may indeed be due to the contribution of hyperfine interactions, which is not treated in our theoretical calculation.

In Tables IV–VI, we present the comparisons of the singlet-triplet level splittings of Be III, B IV, and C V, respectively. Again good agreement is obtained. However, we note the large uncertainties contained in the experimental data. To make comparisons more meaningful, improved experimental data are desirable.

The next group of tables, VII–X, present the fitted parameters for the expressions of ΔE_d and ΔE_{fs} as given in Eqs. (3) and (4). These parameters are determined by least-squares-fitting procedures using the numerically calculated points. With these parameters determined, we can evaluate, for a given Z and L, all level-splittings and level shifts for *all* n values. To examine the accuracy as well as the usefulness of the parametrization procedure, we have calculated directly the level shifts and level splittings ΔE_d and ΔE_{fs} at several *other* (n, Z) values. Comparisons between these calculated values and those derived from our fitted parameters indicate that they agree well within 0.1% for the n fitting and within 0.5% for the Z fitting in the range of n and Z given in this paper. Thus, the three-parameter expansion is well matched to the numerical accuracy of our calculated input values.

Finally, we come to the third group of tables. Here we compare our calculations of the electrostatic singlet-triple level splittings (i.e., without spin-dependent interaction) with other theoretical predictions. In Table XI we have $^1D_2$-$^3D_2$ values for $n=3$ and in Table XII we have the $^1D_2$-$^3D_2$ values for $n=4$ and $n=5$. In Table XIII we present the comparison of $^1F_3$-$^3F_3$ for $n=4$, 5 and 6. Elab-

TABLE XI. Calculated *electrostatic* singlet-triplet level splittings ($^1D_2$-$^3D_2$) for $n=3$ (in 10^{-3} atu).

Z	Weiss[a]	Brown[b]	Blanchard and Drake[c]	Present
2	0.02	0.016	0.01585	0.0155
3	0.16	0.14	0.1365	0.138
4	0.38	0.375	0.3674	0.374
5	0.71	0.68	0.6724	0.684
6	1.07	1.04	1.0256	1.04
7	1.45	1.43	1.4113	1.43
8	1.87	1.84	1.8196	1.85
9	2.29	2.27	2.2442	2.28
10	2.74	2.71	2.6809	2.72

[a] Weiss (Ref. 26).
[b] Brown (Ref. 8).
[c] Blanchard and Drake (Ref. 7).

TABLE XII. Calculated *electrostatic* singlet-triplet level splittings ($^1D_2$-$^3D_2$) for $n=4$ and 5 (in 10^{-3} atu).

	$n=4$			$n=5$	
Z	BC[a]	BD[b]	Present	BC[a]	Present
2	0.01	0.0101	0.00893	0.007	0.00515
3	0.08	0.079	0.0775	0.051	0.0422
4	0.212	0.209	0.207	0.128	0.118
5	0.38	0.376	0.377	0.23	0.213
6	0.58	0.570	0.572	0.34	0.322
7	0.78	0.780	0.783	0.46	0.440
8	1.02	1.002	1.01	0.59	0.565
9	1.24	1.233	1.24	0.72	0.694
10	1.47	1.469	1.47	0.85	0.825

[a] Brown and Cortez (Ref. 9).
[b] Blanchard and Drake (Ref. 7).

TABLE XIII. Calculated *electrostatic* singlet-triplet level splittings ($^1F_3$-$^3F_3$) for $n = 4$, 5, and 6 (in 10^{-6} atu).

	$n=4$		$n=5$		$n=6$	
Z	Brown[a]	Present	Brown[a]	Present	Brown[a]	Present
2	0.04	0.0209	0.04	0.0181	0.02	0.0131
3	0.47	0.412	0.49	0.339	0.37	0.241
4	1.64	2.00	1.57	1.24	1.17	0.879
5	3.43	3.24	3.18	2.67	2.36	1.89
6	5.77	5.49	5.17	4.51	3.82	3.19
7	8.42	8.11	7.44	6.65	5.43	4.70
8	11.37	11.0	9.92	9.01	7.23	6.36
9	14.48	14.1	12.53	11.5	9.08	8.14
10	17.81	17.4	15.26	14.2	11.04	10.0

[a] Brown (Ref. 8).

orate variational approaches using a Hylleraas-type correlated basis set have been employed by Blanchard and Drake[7] and others.[8,26] It is seen that general agreement is obtained in low-n and high-Z cases. However, as n increases, even the elaborate variational calculation began to deteriorate. Our perturbational calculation should continue to yield accurate values, as mentioned earlier, because of its formal cancellation of irrelevant terms.

In conclusion, we have made a detailed and systematic study on the fine structure of the Rydberg states of the helium isoelectronic series. Besides making comparisons with experiments and with other theoretical studies, we have also investigated the general parametrization procedures. It is hoped that this theoretical study will also add impetus to a much more detailed parallel experimental study on the fine structures of the helium isoelectronic sequence.

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