

Energies of $1snl$ ($l \geq 3$) Configurations in He^4 , as Calculated from Polarization Theory

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The calculated singlet-triplet mean energies are given for all He^4 1 configurations having $3 \leq l \leq n-1$ from $4f$ to $8k$. Since only Stark-shifted transitions have been observed for such configurations with $l \geq 4$, the calculated positions are the most accurate available. The polarization energy (to the quadrupole approximation) for two-electron ions may be evaluated for higher nl or Z from the simple formulas. The calculated and observed positions of the $1snf$ configurations in He^4 I and Li^7 II agree within the experimental uncertainties.

Key words: Atomic energy levels; atomic theory; helium; polarizability.

1. Introduction

In a list of He^4 I energy levels published in 1960 [1],¹ positions were given for several configurations $1s5l$, $6l$, $7l$ ($l \geq 4$) that had been observed only in Stark-effect investigations [2]. An attempt was made to derive the approximate undisplaced positions for these configurations from Foster's measurements [2]. However, Foster [3] had already given a more accurate position for the $5g$ configuration relative to the other levels for $n=5$. This position was not derived from his observations but from the polarization theory of term defects due to Born and Heisenberg [4] and Waller [5]. (The "term defect" was the difference between the actual term value and the Bohr energy R/n^2 .) A simple expression for the polarization defect for $1snl$ configurations for $l \geq 3$ is applied here to obtain positions for several such configurations in He^4 I.

2. Polarization Formulas

Polarization theory [4–9] is now frequently used to describe the deviations of non-penetrating terms T in alkali-like atoms from corresponding hydrogenic term values T_0 . For a non-penetrating electron outside a closed-shell core [9]:

$$T - T_0 = \Delta_p = R\alpha_d \langle r^{-4} \rangle + R\alpha_q \langle r^{-6} \rangle \quad (1)$$

where R is the Rydberg constant and α_d and α_q are the electric dipole and quadrupole polarizabilities of the core in units of a_0^3 and a_0^5 , respectively (a_0 is the

Bohr radius). The expectation values $\langle r^{-4} \rangle$ and $\langle r^{-6} \rangle$ have been tabulated [8] and Edlén [9] has given a convenient table for use with the expression²

$$\Delta_p = A(Z)P(n, l)[1 + k(Z)q(n, l)]. \quad (2)$$

Here

$$A(Z) = Z_c^4 \alpha_d \quad \text{and} \quad k(Z) = Z_c^2 \alpha_q / \alpha_d \quad (3)$$

where Z_c is the net charge of the core; $P(n, l)$ and $q(n, l)$ are the quantities tabulated by Edlén.

The polarization energy for an atom with a core having a partly filled shell will in general contain terms not appearing for the closed-shell core. Bethe [10] gives an expression for the polarization quantum-defect for a two-electron atom ($1snl$) that reduces to the dipole value for large $Z \cdot r$.

It is useful to note that Waller's dipole calculation agrees with the current best observations for $1snf$ in both He^4 I and Li^7 II to within the experimental accuracies. Weiss [11] has now shown that the simple expression (1) is valid for $1snl$ configurations of two-electron ions if $l \geq 3$. In this case T is the arithmetic mean of the singlet and triplet terms for $1snl$. This result allows an accurate calculation of Δ_p for such configurations since the $1s$ core polarizabilities are just the hydrogenic values [5, 7]: $\alpha_d = 9/(2Z^4)$ and $\alpha_q = 15/Z^6$. For helium-like ions $Z_c = Z - 1$, and we have from (3):

$$A(Z) = 9(Z - 1)^4 / (2Z^4) \quad (4)$$

$$k(Z) = 10(Z - 1)^2 / (3Z^2). \quad (5)$$

¹Figures in brackets indicate the literature references at the end of this paper.

²An expression having similar form was introduced in [6].

With (4), (5), and (2) the polarization energies for $1snl$ ($l \geq 3$) configurations may be evaluated to the quadrupole approximation for any two-electron ion.

In the case of hydrogenic spectra, T_0 in eq (1) includes the appropriate relativistic correction to the Bohr term [9]. Relativistic corrections for excited states in two-electron ions are not generally available, but calculations for $1snp$ terms ($n=2, 3, 4$) in He I have been reported [12]. The singlet-triplet mean corrections for these terms are of the same order as the relativistic corrections for the corresponding np terms in hydrogen. Since the hydrogenic corrections for $l \geq 3$ are less than 0.01 cm^{-1} , the relativistic corrections for He are probably negligible to the accuracies of the calculations given here. Bethe and Salpeter [13] indicate that the mass-polarization correction is negligible for terms having $l \geq 2$ in two-electron ions. Calculations by Mayer and Mayer [6] show that the effect due to penetration of the $1s$ core by the excited wave function would also be negligible to the accuracy needed here. We thus adopt the uncorrected Bohr energy R/n^2 for T_0 , the mean of the singlet and triplet terms without the Δ_p correction.

3. Term Defects

An accurate value for the He II ($^2S_{1/2}$) series limit is needed in order to obtain (from calculated terms) the positions of the $l \geq 3$ configurations relative to the S , P , and D levels. Seaton [14] applied a least-squares fitting procedure to several observed series and obtained a weighted mean of $198310.76 \pm 0.01 \text{ cm}^{-1}$ for the limit (relative to the He⁴ $1S_0$ ground level at $0.00 \pm 0.15 \text{ cm}^{-1}$) [15].³ His method is a refinement of the usual procedure in that it takes the relation between the quantum defect and the term value explicitly into account in the weighting. He did not, however, give a specific weighting according to the different experimental accuracies. The $3d$, $4d$, $5d$ 1D and $3d-6d$ 3D levels [1, 16] are known to better than 0.01 cm^{-1} , and it should be possible to describe the D series with a simple two-parameter formula. If the $3d$, $4d$, and $5d$ baricenters are fitted to a Ritz formula $n - n^* = a + \beta T$, a limit of $198310.741 \text{ cm}^{-1}$ is obtained. (Here $T = R/n^{*2}$ is the absolute term value, and R for He⁴ is taken as $109722.267 \text{ cm}^{-1}$.) Table 1 gives the results of a Ritz-formula fit⁴ based on Seaton's value for the limit. Comparison of the observed and calculated baricenters for the accurately known lowest three terms shows them to be consistent with this limit. Seaton's method showed convinc-

ingly that the earlier values given for the limit [1, 15] were too high, and his result is adopted here.

TABLE 1. Term values for the $1snd$ ($n=3$ to 8) baricenters in He⁴ I

Calculated values were determined from a Ritz formula with the constants (see text): $R = 109722.267 \text{ cm}^{-1}$; $a = 2.6865 \times 10^{-3}$; $\beta = -5.00 \times 10^{-8}$. Observed values are based on levels from Ref. [1] referred to a limit of $198310.76 \text{ cm}^{-1}$.

$1snd$	n^* (calc)	Term (calc)	Term (obs)	O-C
		cm^{-1}	cm^{-1}	cm^{-1}
$3d$	2.9979239	12208.254	12208.254	0.000
$4d$	3.9976568	6865.683	6865.679	-.004
$5d$	4.997533	4393.225	4393.228	.003
$6d$	5.997466	3050.417	3050.42	.00
$7d$	6.997426	2240.878	2240.92	.04
$8d$	7.997399	1715.526	1715.49	-.04

Table 2 gives the results of an evaluation of (2) for the He⁴ I configurations $1snl$ ($l \geq 3$) to $n=8$. From (4) and (5) the constants are: $A = 9/32$; $k = 5/6$. The limitation on the principal quantum number is arbitrary and the results may be extended to any $1snl$ configuration with $l \geq 3$. It seems unlikely that the approximations in the method give an error as large as 0.1 cm^{-1} even for $4f$ (the largest value of T). The deviations from the observed positions for $5f$ and $6f$ are within the experimental uncertainties. Any reasonable fitting of the nf series by one of the usual series formulas shows the observations for the lowest three members to be inconsistent on the scale of $\sim 0.1 \text{ cm}^{-1}$.

TABLE 2. Calculated polarization defects and term values for some configurations in He⁴ I

The term values and positions are singlet-triplet means. $T_0 = (109722.267/n^2) \text{ cm}^{-1}$, and $T = T_0 + \Delta_p$.

$1snl$	T_0	Δ_p	T	Position ^a	O-C ^b
	cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}
$4f$	6857.642	1.168	6858.810	191451.950	-0.01
$5f$	4388.891	0.673	4389.564	193921.196	.14
$6f$	3047.8408	.413	3048.254	195262.506	.08
$7f$	2239.2299	.269	2239.499	196071.261	.00
$8f$	1714.4104	.184	1714.594	196596.166	.00
$5g$	(see above)	.157	4389.048	193921.712	
$6g$.101	3047.942	195262.818	
$7g$.068	2239.298	196071.462	
$8g$.047	1714.457	196596.303	
$6h$.032	3047.873	195262.887	
$7h$.022	2239.252	196071.508	
$8h$.016	1714.426	196596.334	
$7i$.009	2239.239	196071.521	
$8i$.006	1714.416	196596.344	
$8k$.003	1714.413	196596.347	

³ Pekeris calculated a value of $198310.674 \pm 0.025 \text{ cm}^{-1}$ for the principal ionization energy of He [Phys. Rev. **126**, 1470 (1962)]. If this result is accepted, the $1S_0$ ground level is at $+0.086 \pm 0.025 \text{ cm}^{-1}$ relative to the positions as given here and in [1] for all excited configurations. An additional uncertainty that varies from $< 0.01 \text{ cm}^{-1}$ to $> 0.1 \text{ cm}^{-1}$ is then associated with the excited levels. The term values calculated here with respect to the limit are not affected by any such change in the ground level.

⁴ The series constants (from table 1) give $R\beta/a = -2.04$, quite close to the value -2.00 expected if a and β were entirely due to the dipole polarizability α_d . The D terms deviate from the positions predicted by the hydrogenic $1s$ core value for α_d , however, by about 6 percent of the term defects. Weiss [11] finds that the polarization energy for $1snd$ includes terms in addition to the two polarizability terms in eq (1) above. The only available polarization-theory method that will accurately predict the nd terms is to fit the low terms by treating the limit, $A(Z)$, and $k(Z)$ as adjustable parameters [9]. Such a fit for the $3d$, $4d$, $5d$ baricenters gives $A = 0.27840$ and $k = 0.021$. The calculated limit and all calculated terms then agree to within 0.002 cm^{-1} with corresponding values obtained from fitting the same three terms to the Ritz formula.

^a Relative to the $1s^2 1S_0$ ground level at $0.00 \pm 0.15 \text{ cm}^{-1}$. (Position) = $198310.760 \text{ cm}^{-1}$ - T ; this limit is thought to be accurate to $\pm 0.01 \text{ cm}^{-1}$.
^b Difference between the observed [Ref. 1] and calculated positions.

It could well be that the $5f$ and $6f$ positions are mainly at fault, as indicated by the deviations in table 2.

The $nf\ ^1F^\circ - ^3F^\circ$ separations obtained from the experimental positions for $4f$ and $5f$ (0.28 and 0.06 cm^{-1} , respectively) [1] are almost surely due to observational error (perhaps including source effects). The calculated separations [17] of only 0.011 and 0.009 cm^{-1} , respectively, should be accurate to much better than an order of magnitude. Thus at least one of the $4f$ terms is in error by more than 0.1 cm^{-1} , and an error of 0.2 cm^{-1} in the mean seems reasonable.

If the various terms are known experimentally to about the same accuracy (in cm^{-1}), the most sensitive comparisons with polarization calculations for $l \geq 3$ are obtained with the lowest nf configurations. The "O-C" results for these configurations in table 2 thus confirm the dipole contribution to the term defect to about 20 percent. They are not accurate enough to check the quadrupole contribution, however, which amounts to only about 2 percent of the dipole correction.

Any errors in T due to the approximations become smaller (in cm^{-1}) for higher values of n . Term values with more than three decimal places would be required in table 2 to give some separations of the higher configurations to the probable accuracy of the method.

The positions (relative to the ground level) previously given by the author [1] for the g , h , and i configurations in He are too high by up to 0.8 cm^{-1} (for $5g$). They are, in fact, unphysical in that they are *above* the corresponding Bohr positions. The best values now available for these configurations, and those of still higher l , are obtained from the polarization theory.

The calculated polarization energy for $l = 3$ is confirmed by the low F terms [18] in Li^7II to a somewhat better percentage accuracy than the available measurements allow for He^4I . In table 3 we see that the term defects for Li^7II nf configurations are about three times the corresponding values for He^4I . The experimental uncertainty⁵ for the lower F terms in LiII is probably about 0.2 cm^{-1} . The calculated and experimental term defects thus agree to within the experimental accuracy, and calculated values different by more than ~ 10 percent would not agree with the observations. The values given for T_0 in table 3 are themselves uncertain by at least 5 percent, because relativistic effects are not included.⁶ The total uncertainty in $T_0 - T_{\text{obs}}$ for these terms is thus about three times the ~ 4 percent quadrupole contribution to Δ_p .

We see from eq (5) for $k(Z)$ that the quadrupole contribution rises with Z ; for high Z , $k(Z) \rightarrow 10/3$ and $A(Z) \rightarrow 9/2$. The polarization energies for a particular

term thus approach asymptotic values with increasing Z . The quadrupole contribution for $4f$ approaches 6.9 percent, and the total polarization defect approaches (18.37 + 1.28) $\text{cm}^{-1} = 19.65 \text{ cm}^{-1}$. However, the realistic corrections to T_0 are expected to increase as $(Z - 1)^4$. These corrections (see footnote 6) are probably already of the same order as the quadrupole energy for $1snf$ in LiII . It appears that verification of the quadrupole term for $1snf$ in two-electron ions would require a calculation of the relativistic effects.

TABLE 3. Calculated and observed term defects for $1snf$ configurations in Li^7II .

The polarization constants for Δ_p are $A = 8/9$ and $k = 40/27$. Term values are singlet-triplet means (see footnote 5). $T_0 = 4R/n^2 = (438914.91/n^2) \text{ cm}^{-1}$.

$1snf$	T_0	T_{obs}	$T_0 - T_{\text{obs}}$	Δ_p
	cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}
$4f$	27432.18	27435.78	3.60	3.74
$5f$	17556.60	17558.69	2.09	2.16
$6f$	12192.08	12193.35	1.27	1.33
$7f$	8957.45	8958.3 ₂	0.8 ₇	0.87
$8f$	6858.05	6858.6 ₈	.6 ₃	.59
$9f$	5418.70	5419.1 ₈	.4 ₈	.42
$10f$	4389.15	4389.3 ₃	.1 ₈	.31

Note added in proof: Another effect neglected here is also probably comparable in magnitude to the quadrupole-polarization energy, even in HeI . A very recent paper giving polarization energies in HeI [C. Deutsch, Phys. Rev. A **2**, 43 (1970)] includes a nonadiabatic correction calculated to be slightly larger than, and opposite in sign to, the quadrupole-polarization contribution.

A. W. Weiss has been very helpful in discussions about two-electron atoms. I am especially grateful for his making available a new derivation that gives a firm theoretical basis for eq (1) as used here. A private letter from William S. Cooper, III, questioning (on the basis of AC Stark-effect observations) the $5g$ position given in [1] stimulated me to examine the accuracy of polarization theory for two-electron atoms.

4. References

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⁵ The calculated singlet-triplet separations of the F terms in LiII are only 0.15 and 0.13 cm^{-1} for $4f$ and $5f$, respectively [17]. These are not observed, being much smaller than the resolved hyperfine splittings of $\sim 1.0 \text{ cm}^{-1}$ [18]. On the assumption that the baricenter of the hyperfine structure is also the 3F , 1F baricenter, the singlet-triplet means (T_{obs}) in table 3 were made less than the corresponding baricenter term values by small amounts (0.04 cm^{-1} for $4f$ to 0.01 cm^{-1} for $8f$ and $9f$). Term determinations with respect to the limit baricenter were made by using the $2s^2S_1$ baricenter at $134044.19 \pm 0.10 \text{ cm}^{-1}$ [18]. An uncertainty of 0.2 cm^{-1} for the lower F terms is probably sufficient to include the additional error due to uncertainty in their positions with respect to $2s^2S_1$.

⁶ Relativistic corrections have been calculated for LiII $2p\ ^1P$ [12]. The LiII $1snf$ corrections are probably of the order of the corresponding HeII nf corrections, equal to 0.14 cm^{-1} for $4f$.

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