Ge (^1D) and O (^3P). The electronic transitions $^1\Pi \rightarrow {}^1\Sigma$ and $^1\Sigma \rightarrow {}^1\Sigma$, are therefore possibilities. A comparison of the values of ν_e of the fourth column monoxides shows that the $^1\Pi \rightarrow {}^1\Sigma$ transition is the more likely. The observed band system of GeO is then similar to the fourth positive system of CO.

It is interesting to note that the quantity, $\omega_e'' r_e^2 \cdot 10^{-16}$ cm, as evaluated from the data on CO, SiO and PbO, is very nearly a constant. The essential data, which are given in Table III, show that the deviations of individual values from the mean, 2742.3 cm, are less than three percent. This produces in the case of a calculated value of r_e for PbO a deviation of 0.02 unit or about one percent which is within usual experimental error in determinations of r_e. The corresponding calculated values of r_e for GeO and SnO are 1.69A and 1.82A, respectively. The internuclear distance 1.69A for GeO is in good agreement with the Ge–O distance, 1.65A, observed by Warren[6] in GeO_2.

It is well known[7] that there is only a small change in the C–O distance[8] in CO_2 (1.05–1.2A depending on the physical state) and CO (1.13A) and in SiO_2 (1.60A) and SiO (1.50A). Moreover, while the character of binding gradually changes as one goes downward in a periodic column as is shown by chemical properties, it has not varied so greatly at germanium that one would expect any pronounced peculiarities of internuclear distance. It seems reasonable, therefore, to consider 1.65 ± 0.06A as a good value of r_e for GeO pending the possibility of a rotational analysis of some of the individual bands.

The author wishes to express appreciation to Professor R. C. Gibbs for his interest in the problem and to Professor A. W. Laubengayer of the Chemistry Department for supplying the GeO_2 and for many helpful discussions on the properties of the oxides of the fourth periodic column.

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[6] B. E. Warren, Phys. Rev. **45**, 657 (1934).

[7] R. Kronig, *Optical Basis of the Theory of Valency* (1935), p. 164.

[8] H. A. Stuart, *Molekulstruktur* (1934), p. 77.

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Helium I Like Spectra

Howard A. Robinson,* *University of Uppsala, Sweden*

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New measurements of the $1s^2\,{}^1S_0 - 1s\cdot np\,{}^1P_1$ series of the Helium I isoelectronic sequence for Be III, B IV and C V together with previously published data on He I, Li II, N VI and O VII are critically examined and values for the $1s^2\,{}^1S_0$ terms for these spectra obtained. A slightly modified Hylleraas type extrapolation formula is used to calculate these same values. When relativity, spin, mass and mass polarization corrections are applied the agreement between observed and calculated values is very good for the heavier elements. A small discrepancy appears in the case of Li II.

It has been possible for some time to calculate the ground states of the helium I like spectra by means of the formulae first given by Hylleraas.[1] The experimental data have, however, been meager due mainly to the inaccessibility of the region below 100A where most of the necessary lines lie. A new 4° grazing incidence spectrograph designed by Professor Siegbahn[2] and built in the workshops of this institute has proved unusually well suited to this region and it is now possible for the first time to measure lines below 100A with an accuracy of a few thousandths of an angstrom. The spectra Li II, Be III, B IV, and C V are, in addition, useful as wave-length

Table I. *Data for* Li II.

n	2	3	4
λ (A)	199.280 ± 0.003	178.014 ± 0.003	171.575 ± 0.004
ν cm^{-1}	$501{,}807 \pm 5$	$561{,}754 \pm 10$	$582{,}835 \pm 14$
T cm^{-1}	$108{,}263 \pm 10$	$48{,}330 \pm 3$	$27{,}247 \pm 4$
$1s^2\,{}^1S_0$ =	$610{,}070 \pm 15$	$610{,}084 \pm 13$	$610{,}082 \pm 18$
$1s^2\,{}^1S_0 = 610{,}079 \pm 25$ cm^{-1}		I.P. $= 75{,}2593 \pm 0.0031$ volts	

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* Irving Langmuir Fellow, American Scandinavian Foundation. Now at Ohio State University.

[1] E. Hylleraas, Zeits. f. Physik **65**, 209 (1930).

[2] B. Edlén, Zeits. f. Physik **100**, 621 (1936).

standards between 200A and 33A, particularly when used in conjunction with the hydrogen like spectra of the same elements the lines of which may be calculated exactly by means of Penney's[3] formula. The wave-lengths as presented in this paper have been measured in several orders using the hydrogen like spectra or known oxygen lines as standards. The beryllium III measurements have been described separately.[4] The measurements for boron IV are from unpublished data of B. Edlén and are included here for completeness through the kindness of Docent Edlén. The measurements for carbon V are the averages of measurements made by Docent Edlén and the author on a series of individual plates. While in all cases the maximum deviation from the mean of the higher orders and all measurements on the individual lines was in the maximum case ±0.003A it is nevertheless felt that the higher series measurements may be in error by ±0.005A. The error in the first two members should, however, be less than this latter value due to the many high order measurements involved. The higher series lines are furthermore apt to be diffuse, but this effect appears to be less marked as the atomic number increases.

The discussion which follows should be considered as supplementary to that of Bethe[5] the notation used here being the same as in that article. Several small numerical errors have been corrected. Most of these are in Bethe's Table 7 (page 363) where the relativity corrections for Li II, Be III, B IV and C V are incorrectly given. The calculated energies for the ground state are therefore also in error. Bethe's Table 11 (page 384) is essentially correct except for small deviations in the last unit in certain cases. This deviation, however, is beyond the accuracy of the calculation and therefore of no importance.

TABLE II. *Data for Be III.*

n	λ (A)	ν cm^{-1}	$1s\cdot np\ ^1P_1$	n^*
2	100.254±0.001	997,466±10	243,759	2.01282±0.00037
3	88.314± .002	1,132,323±25	108,902	3.0114
4	84.758± .003	1,179,830±40	61,395	4.0107
5	83.202± .003	1,201,894±43	39,331	5.0109
6	82.377± .004	1,213,931±60	27,294	6.0107
7	81.891± .005	1,221,135±75	20,090	7.0103

$1s^2\ ^1S_0=1,241,225\pm100$ cm^{-1} I.P. $=153.118\pm0.012$ volts

TABLE III. *Data for B IV.*

n	λ (A)	ν cm^{-1}	$1s\cdot np\ ^1P_1$	n^*
2	60.313±0.002	1,658,017± 60	433,943	2.01145±0.00051
3	52.679± .002	1,898,290± 72	193,670	3.0109
4	50.435± .003	1,982,750±120	109,210	4.0096
5	49.456± .005	2,021,999±205	69,961	5.0095

$1s^2\ ^1S_0=2,091,960\pm300$ cm^{-1} I.P. $=258.064\pm0.034$ volts

TABLE IV. *Data for C V.*

n	λ (A)	ν cm^{-1}	$1s\cdot np\ ^1P_1$	n^*
2	40.270±0.001	2,483,238± 65	679,212	2.00972±0.00089
3	34.973± .002	2,859,347±165	303,101	3.0085
4	33.426± .003	2,991,683±275	170,677	4.0081
5	32.754± .005	3,053,062±500	109,388	5.0079

$1s^2\ ^1S_0=3,162,450\pm600$ cm^{-1} I.P. $=390.120\pm0.074$ volts

THE EXPERIMENTAL DATA

Helium I

The ground state of this spectrum has been treated by Paschen.[6] The higher states are well known because of accurate measurements in more accessible regions and Paschen was able by means of a spectrogram taken by Kruger to evaluate the ground state by means of its eleven combinations with the lowest eleven $1s\cdot np\ ^1P_1$ terms ($n=2$ to 12) already known. Paschen's[7] final value is $1s^2\ ^1S_0=198,305$ cm^{-1}. Since the values are consistent to within ±10 cm^{-1} we may assume that the value is accurate to ±15 cm^{-1} (especially if we consider that the absolute value of the terms may also be in error by a few centimeters^{-1}).

$$1s^2\ ^1S_0=198,305\pm15\ \text{cm}^{-1},$$
$$I.P.=24.4633\pm0.0019\ \text{volts}.$$

Lithium II

The higher states for Li II are known from the work of Schüler and Werner,[8] as in the He I case, but with much less accuracy. The $1s^2\ ^1S_0-1s\cdot np\ ^1P_1$ series appears to be difficult to excite as several long exposures have failed to reveal more than the first three or four members. The values in Table I are from the data of Docent Edlén but differ somewhat from his previously published values.[9] The term values are those of Werner.

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[3] W. G. Penney, Phil. Mag. **9**, 661 (1930).

[4] H. A. Robinson, Phys. Rev. **50**, 99 (1936).

[5] H. Bethe, *Handbuch der Physik*, Vol. 24/1, p. 324 et seq.

[6] F. Paschen, Preussische Akad. der Wiss. Sitzungsber. Seite 662 (1929).

[7] Data from correspondence between Professor Paschen and the author. I am extremely indebted to Professor Paschen for his kindness in this matter.

[8] S. Werner, *Studier over Spektroskopiske Lyskilder* (Copenhagen, Dissertation 1927).

[9] B. Edlén, *Nova Acta Regiae Soc. Scient.* Vol. 9, No. 6 (Uppsala, 1933).

The errors in the latter are those assigned by that author.

Beryllium III

Data for the higher terms have never been published and as a result one must depend on the $1s^2\,{}^1S_0 - 1s\cdot np\,{}^1P_1$ series for an evaluation of the limit. The data are given in Table II.

The error in the absolute value of the ground state has been calculated as in the following spectra by assuming the maximum error in each wave-length and recalculating the limit under these new conditions: The error in n^* is that due to the error in the limit.

Boron IV

The only available data are those for the $1s^2\,{}^1S_0 - 1s\cdot np\,{}^1P_1$ series. The measurements are given in Table III.

Carbon V

The $1s^2\,{}^1S_0 - 1s\cdot np\,{}^1P_1$ series of carbon V is given in Table IV.

This series has been measured by F. Tyrén[10] in this institute using a 5-meter concave grating and a plate perpendicular to the diffracted rays. The measurements made by this method are inherently less accurate than those made by the grazing incidence method, primarily because the dispersion is about six times as large in this latter case. For the lines given the check between Tyrén's values and these is satisfactory. The three higher members as measured by Tyrén alone show, however, rather considerable variation in the quantum defect, as calculated using the above limit, as follows:

$$\begin{array}{rr} n=6 & n^*=6.0069 \\ 7 & 7.0178 \\ 8 & 7.7924. \end{array}$$

Since the accuracy of these latter three lines is so much below that of the first four members of the series they have not been considered in calculating the limit.

Nitrogen VI and oxygen VII

Tyrén[10] has observed the first lines in these series ($1s^2\,{}^1S_0 - 1s\cdot 2p\,{}^1P_1$) at 28.787A and 21.615A, respectively. In order to obtain an estimate of the accuracy of these measurements we may extrapolate $\nu - RZ^2\cdot\frac{3}{4}$ for this line as follows:

	ν measured		*ν extrapolated*	
He I	88,292			
		89,795		
Li II	172,615			
		84,169		
Be III	256,784			
		84,449		
B IV	341,233		341,233	
		84,608		84,608
C V	425,841		425,841	
		85,152		[84,900]
N VI	510,993		[510,740]	
		82,713		[85,200].
O VII	593,706		[595,940]	

We thus see that the N VI line ν value is possible 250 cm^{-1} too large, but that the O VII line ν value is in error by approximately 2000 cm^{-1}. The extrapolation in this latter case is rather more accurate because of the position of the line itself with respect to standards. We may therefore take for N VI

$$\nu_{{}^1S_0 - {}^1P_1} = 3{,}473{,}790 \pm 400 \text{ cm}^{-1} \quad \lambda = 28.787 \pm 0.004$$

and for O VII

$$\nu_{{}^1S_0 - {}^1P_1} = 4{,}627{,}900 \pm 1500 \text{ cm}^{-1} \quad \lambda = 21.608 \pm 0.007$$

where the latter value refers to a weighted mean between extrapolation and observed values. We may furthermore extrapolate by Moseley's law to obtain a value for $1s\cdot 2p\,{}^1P_1$ as follows:

	ν	$\sqrt{\nu}$	$\Delta\sqrt{\nu}$
He I	27,176	164.85	
			164.19
Li II	108,268	329.04	
			164.68
Be III	243,759	493.72	
			165.02
B IV	433,943	658.74	
			165.40
C V	679,212	824.14	
			[165.82]
N VI	[979,880]	[989.89]	
			[166.28]
O VII	[1,336,320]	[1155.99]	

Using these values we get for the ground states:

$$\begin{array}{ll} \text{N VI} & 1s^2\,{}^1S_0 = 4{,}453{,}670 \pm 1500, \\ & \text{I.P.} = 549.41 \pm 0.18 \text{ volts.} \\ \text{O VII} & 1s^2\,{}^1S_0 = 5{,}964{,}200 \pm 2500, \\ & \text{I.P.} = 735.74 \pm 0.31 \text{ volts.} \end{array}$$

THE CALCULATION OF THE GROUND STATES

The Hylleraas calculation for the gound states of these ions consists essentially of two parts. Calculations were first made of the absolute value of the ionization potential for the negative

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[10] F. Tyrén, Zeits. f. Physik **98**, 768 (1936).

hydrogen ion (H^-) and for He I by means of the Ritz variational method carried to high approximations. The Schrödinger equation was then solved by means of a perturbation calculation involving the energies in terms of a series in powers of $1/Z$. Hylleraas succeeded in calculating the first three coefficients of this series. Because the values for the first two members (H^- and He I) of the isoelectronic sequence were known (from the first part of the Hylleraas calculation) it was possible to solve for two more coefficients. A recent, as yet unpublished, calculation of the Li II ionization potential by Mr. H. A. S. Eriksson of this university shows in the 12th approximation a small deviation in the last place from the value calculated by means of the Hylleraas formula. If we use the Eriksson value for Li II it is now possible to find one more coefficient in the expansion of $1/Z$ and thus to slightly modify the Hylleraas formula. The final result is

$$J=\left[Z^2-\frac{5}{4}Z+.31488-\frac{.01710}{Z}+\frac{.00422}{Z^2}+\frac{.00084}{Z^3}\right]R_Z. \quad (1)$$

This formula, which gives slightly larger values for the ground state than does the original Hylleraas formula, has been used in this paper.

The values obtained from (1) are to be corrected for several effects not considered in the original derivation. The first of these H_1 arises from the relativistic change of mass with velocity. The second of these H_4 arises from a characteristic term in the Dirac Theory and in the one electron problem is known as the spin correction for s terms. These corrections can be calculated when the respective wave functions are known. They have been calculated by Bethe[11] using the simple first approximation wave functions $u=e^{-(Z-5/16)(r_1+r_2)}$. The results are for a *two* electron case

$$H_1=-5/2(Z-5/16)^4\alpha^2R, \quad (2)$$

$$H_4=+2(Z-5/16)^3(Z-1/8)\alpha^2R. \quad (3)$$

Since we are considering calculations of ionization potentials (which are the differences in energy between the zth and the $(z-1)$ ion) H_1 and H_4 must have subtracted from them, in order to be applicable to our problem, the corresponding correction for the ion with one electron (H_i).

$$H_i=-\tfrac{1}{4}Z^4\cdot\alpha^2\cdot R. \quad (4)$$

These three corrections taken together must be considered as only first approximations due to the simple manner of their calculation. The values are listed in Table V.

In addition to the previously discussed relativity correction we have certain mass corrections to be considered. Deviating from Bethe's treatment we shall here use the value of R_Z[12] corresponding to each individual element instead of multiplying by R_∞ and applying a correction. There is, however, very small polarization mass correction ϵ_3 which as Bethe[13] has shown amounts to 5.2 cm⁻¹ in the case of helium. In an effort to approximate this correction for the higher ions a calculation has been made by using the Hylleraas wave function with eight terms. (Bethe, Eqs. (18.9), (18.24) and (18.30)) and evaluating the integral given by Bethe on page 375. The result is

$$\epsilon_3=\frac{m}{M}Z^2\left[\frac{0.03359Z-0.20054}{0.77539+0.56283Z+0.12499Z^2}\right]. \quad (5)$$

TABLE V. *Relativity corrections.*

	He I		Li II	Be III	B IV	C V	N VI	O VII
	A.	B.						
H_1 relativity	+19.4	+20.3	+130.4	+462.2	+1207.0	+2615.9	+5000.3	+8731.3
H_4 spin	−20.1	−18.0	−111.6	−388.6	−1004.2	−2161.7	−4112.4	−7155.4
H_i ion	− 4	− 4	− 20.3	− 64.0	− 156.3	− 324.0	− 600.3	−1024.0
Total (α^2R)	− 4.7	− 1.7	− 1.5	+ 9.6	+ 46.5	+ 130.2	+ 287.6	+ 551.9
Total (cm⁻¹)	−27	−10	− 8	+ 56	+ 272	+ 760	+1680	+3223

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[11] Reference 5, page 384.

[12] Values of R_Z taken from White, *Introduction to Atomic Spectra*, p. 38.

[13] Reference 5, page 375.

TABLE VI. *Mass polarization corrections.*

	He I		Li II		Be III	B IV	C V	N VI	O VII
	A.	B.	A.	B.					
ϵ_3	$-0.17\,m/M$	$-0.22\,m/M$	$-0.10\,m/M$	$-0.25\,m/M$	$-0.21\,m/M$	$-0.12\,m/M$	$+0.005\,m/M$	$+0.16\,m/M$	$+0.33\,m/M$
(cm^{-1})	−5.2	−6.6	−1.7	−4.3	−2.7	−1.4	+ .07	+1.3	+2.4

TABLE VII. *Compilation of results for various spectra.*

ELEMENT	HYLLERAAS MOD.	RELATIVITY CORRECTION	MASS POLARIZ. CORRECTION	TOTAL		TOTAL*	
				CALCULATED	EXPERIMENTAL	VOLTS (CALCULATED)	VOLTS (EXPERIMENTAL)
He I	198,322 cm^{-1}	(A) −27 cm^{-1}	−5 cm^{-1}	198,290 cm^{-1}		(A) 24.4611	
		(B) −10	−5	198,307	198,305 ± 15 cm^{-1}	(B) 24.4632	24.4633 ± 0.0019
Li II	610,057	−8	−4	610,045	610,079 ± 25	75.2552	75.2593 ± .0031
Be III	1,241,151	+56	−3	1,241,204	1,241,225 ± 100	153.1149	153.118 ± .012
B IV	2,091,672	+272	−1	2,091,943	2,091,960 ± 300	258.0621	258.064 ± .034
C V	3,161,629	+760	0	3,162,389	3,162,450 ± 600	390.1124	390.120 ± .074
N VI	4,451,055	+1680	+1	4,452,736	4,453,700 ± 1500	549.2895	549.41 ± .18
O VII	5,959,945	+3223	+2	5,963,170	5,964,200 ± 2500	735.6168	735.74 ± .31

* In all calculations in this paper the factor 1.2336×10^{-4} has been used in changing cm^{-1} to electron volts.

The values are listed in Table VI.[14] It will be seen that with the possible exception of the values for He I and Li II these corrections are unimportant.

FINAL RESULTS

In Table VII the final results are shown. The two relativity corrections for He I are (A) calculated by Bethe using Hartree eigenfunctions and (B) calculated using Eqs. (2), (3) and (4).

The final results show, on the whole, remarkably good agreement but the following points should be noticed.

I. In the case of Li II there appears to be a small but real difference between the theoretical and observed value for $1s^2\,{}^1S_0$.

II. The experimental values lie without exception slightly higher than do the calculated values. This difference is to be expected from a variation method as the latter should lead to slightly too low a value for the ionization potential.

III. The Eriksson calculation shows that the Hylleraas extrapolation formula cannot be markedly changed by the calculation of higher members of the isoelectronic series. As a result a more exact calculation of the relativity and mass corrections should be carried through at least for the Li II case in order to determine if there be in reality a small, as yet unaccounted for, residual effect.[15]

I wish to take the opportunity to thank Professor Siegbahn for his extreme kindness in placing the necessary apparatus at my disposal and for the generous manner with which he has met every request. Professor Ivar Waller has been extremely kind in discussing the latter part of the paper with me.

Docent Bengt Edlén, aside from allowing me to publish part of his own data, has critically examined the whole of the experimental results while Mr. Eriksson has allowed me free use of his own calculations on lithium II prior to their publication. I should also like to thank the American Scandinavian Foundation for its part in making my stay in Uppsala possible.

Note added in proof: Since writing the above Mr. Eriksson has kindly forwarded his complete results on the relativity corrections for Li II. The values given in Table V may now be replaced by the following

H_1	H_4	H_i	Total (α^2R)	Total (cm^{-1})
+153.8	−125.1	−20.3 (calc. from (4))	+8.4	+49

The calculated value for the ground state is thus 610,102 cm^{-1} which checks with the experimental result within the limit of error. It should be noted, however, that this case is an exception to conclusion II stated above.

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[14] In this table the two values for He and Li refer (A) to the evaluation of ϵ_3 using the helium (Li) eigenfunction (Bethe, page 375) and (B) to the evaluation of ϵ_3 using 5. A more careful calculation should be made before one can decide whether the change in sign beginning with C V is real.

[15] This is now being done by Mr. Eriksson. Since the total correction in this case is the difference of two practically equal quantities the rough calculation made using Eqs. (2) and (3) would not be expected to be at all accurate. From the experimental data one should expect the correction to be positive instead of negative. Mr. Eriksson's preliminary results show that H_1 is given in Table V is actually too small, with the result that the discrepancy is probably due to the error in the "correction."