

sition of Li II can be expressed as the sum of a Lamb shift in the $2s^3S$ state of -0.99 cm^{-1} and a Lamb shift in the $2p^3P$ state of $+0.28 \text{ cm}^{-1}$. Previous measurements in other transitions in two-electron atoms verify our predictions.

Although the 3P Lamb shifts produce good agreement between theory and experiment, we must admit the possibility of two other explanations for the observed Lamb shifts. The first is an increase of the theoretical n^3S Lamb shifts by 20%. This is unlikely, especially for the $2s^3S$ state of He I, where the estimated precision of Suh and Zaidi⁴ is 10%. However, a similar discrepancy arises in the $1s^2^1S$ Lamb shift of C V, as pointed out by Edlén and Löfstrand.² The observed Lamb shift is $-178 \pm 30 \text{ cm}^{-1}$, while theory¹⁸ gives -132 cm^{-1} . The discrepancy could be considered as just within the bounds

of the combined experimental and theoretical error limits. This leads us to another possible source of error. The total energies of the S states of two-electron atoms, as calculated by Pekeris¹⁸ and Accad *et al.*³ might be too high—by this small factor, which is proportional to Z^4/n^3 , thus creating a spurious S-state “Lamb shift.”

The principal exception to these last two possibilities is the close agreement between theory and experiment for the $2s^1S - 2p^1P$ transition in He I, and to a lesser extent in C V. The most reasonable explanation is to assume a very small Lamb shift for the 1P terms.

A calculation of the $2p^3P$ Lamb Shift in He I and Li II would be invaluable for comparison with experiment. We hope to improve our precision for the measurements in Li II and also to remeasure the $2s^3S - 2p^3P$ transition in He I.

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Nuclear-Charge-Expansion Method for $(2s^a 2p^b - 2s^{a-1} 2p^{b+1})$ Transitions*

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The nuclear-charge-expansion method is used to calculate the radiative probabilities of the dipole transitions $2s^a 2p^b - 2s^{a-1} 2p^{b+1}$ of ionic systems. An extensive comparison with more-elaborate calculations and with experimental data shows that after a few stages of ionization the method gives results of uniformly high accuracy.

I. INTRODUCTION

The nuclear-charge-expansion method has been used by several authors to calculate atomic transition probabilities for isoelectronic sequences. Precise calculations performed so far have been limited to the helium¹⁻³ and lithium⁴⁻⁵ sequences,

although other systems have been examined in the Hartree-Fock approximation.⁶⁻⁸ The Hartree-Fock approximation gives the leading term in the expansion of the transition probability in powers of Z^{-1} correctly, but not the second term. The second term can be calculated exactly provided zero-order mixing does not occur. In this paper

we calculate matrix elements of the electric dipole transition operator correct to first order in the perturbation, for $2s$ - $2p$ transitions of the form $1s^2 2s^a 2p^b - 1s^2 2s^{a-1} 2p^{b+1}$ for those levels for which zero-order mixing does not occur, and employ experimental energy differences to obtain the corresponding transition probabilities. In an extensive tabulation the results are compared with other calculations and with the available experimental data obtained mainly from beam-foil lifetime measurements.

II. Z EXPANSION OF DIPOLE MATRIX ELEMENTS FOR N -ELECTRON SYSTEMS

Consider an N -electron atomic system with nuclear charge Z . The Z -expansion method is developed by choosing the unit of length to be Z^{-1} a.u. and the unit of energy to be Z^2 a.u. so that the non-relativistic atomic Hamiltonian H can be written as

$$H = H_0 + (1/Z)H_1,$$

where

$$H_0 = \sum_{i=1}^N \left(-\frac{1}{2} \nabla_i^2 - \frac{1}{r_i} \right),$$

$$H_1 = \sum_{i < j}^N \frac{1}{r_{ij}},$$

and \vec{r}_i is the position vector of the i th electron. The eigenfunctions of H can then be written as a perturbation expansion

$$\Psi = \Psi_0 + (1/Z)\Psi_1 + \dots$$

For our purposes it is convenient to follow Chisholm and Dalgarno⁹ and write, using a LS -cou-

TABLE I. Zero-order and first-order reduced-transition-matrix elements for heliumlike systems.

Transition	Zero-order matrix element	First-order matrix element
$1s2s \ ^1S - 1s2p \ ^1P$	$3\sqrt{3}$	$\frac{19\ 997\sqrt{3}}{3^3}$
$1s2s^3S - 1s2p \ ^3P$	$3\sqrt{3}$	$\frac{14\ 941\sqrt{3}}{3^3}$
$2s2p \ ^1P - 2p^2 \ ^1D$	$3\sqrt{10}$	$\frac{-73\sqrt{10}}{640}$
$2s^2 \ ^1S - 2s2p \ ^1P$	$3\sqrt{6}$	$\frac{51\sqrt{6}}{64}$
$2p^2 \ ^1S - 2s2p \ ^1P$	$-3\sqrt{2}$	$\frac{73\sqrt{2}}{64}$
$2s2p \ ^3P - 2p^2 \ ^3P$	$3\sqrt{6}$	$\frac{73\sqrt{6}}{128}$

pling scheme, the zero-order eigenfunctions Ψ_0 in the form

$$\Psi_0(\Gamma L S | N) = \sum_{\Gamma_1 L_1 S_1} \sum_{\Gamma_2 L_2 S_2} (\Gamma_1 L_1 S_1, \Gamma_2 L_2 S_2 | \Gamma L S) \times \{ \Psi_0(\Gamma_1 L_1 S_1 | 2), \Psi_0(\Gamma_2 L_2 S_2 | N-2) \}, \quad (1)$$

where $\{ \Psi_0(\Gamma_1 L_1 S_1 | 2), \Psi_0(\Gamma_2 L_2 S_2 | N-2) \}$ is a vector-coupled product of normalized antisymmetric two-electron eigenfunctions $\Psi_0(\Gamma_1 L_1 S_1 M_{L_1} M_{S_1} | 2)$ and normalized antisymmetric $(N-2)$ -electron eigenfunctions $\Psi_0(\Gamma_2 L_2 S_2 M_{L_2} M_{S_2} | N-2)$, and $(\Gamma_1 L_1 S_1, \Gamma_2 L_2 S_2 | \Gamma L S)$ is a two-particle fractional parentage coefficient. Ψ_1 , which satisfies the equation

$$(H_0 - E_0) \Psi_1 + (H_1 - E_1) \Psi_0 = 0, \quad \langle \Psi_0 | \Psi_1 \rangle = 0,$$

can be written

$$\Psi_1 = A \sum_{\Gamma_1 L_1 S_1} \sum_{\Gamma_2 L_2 S_2} (\Gamma_1 L_1 S_1, \Gamma_2 L_2 S_2 | \Gamma L S) \times \{ \Psi_1(\Gamma_1 L_1 S_1 | 2), \Psi_0(\Gamma_2 L_2 S_2 | N-2) \},$$

where A is the antisymmetrizing operator and $\Psi_1(\Gamma_1 L_1 S_1 | 2)$ is a first-order two-electron eigenfunction

$$\left(-\frac{1}{2} \nabla_1^2 - \frac{1}{2} \nabla_2^2 - 1/r_1 - 1/r_2 - E_0 \right) \Psi_1(\Gamma_1 L_1 S_1 | 2) + (1/r_{12} - E_1) \Psi_0(\Gamma_1 L_1 S_1 | 2) = 0. \quad (2)$$

It then follows that, through first order in the perturbation, an off-diagonal reduced-matrix element of a one-electron operator $\tilde{Q}_\lambda(N) = \sum_{i=1}^N q(i)$ is a linear combination of two-electron reduced-

TABLE II. Zero-order (I_0) and first-order (I_1) coefficients in the Z expansion of the reduced dipole transition-matrix element for $1s^2 2s^a 2p^b - 1s^2 2s^{a-1} 2p^{b+1}$ transitions. $\sigma_1 = 32\ 410/3^9$, $\sigma_2 = 73/1920$, and $\sigma_3 = 17/64$.

N	a	b	Transition	I_0	I_1/I_0
3	1	0	$^2S - ^2P$	$3\sqrt{3}$	σ_1
4	1	1	$^3P - ^3P$ $^1P - ^1D$	$3\sqrt{6}$ $3\sqrt{10}$	$\sigma_1 + 5\sigma_2$ $\sigma_1 - \sigma_2$
5	1	2	$^4P - ^4S$ $^2D - ^2D$ $^2P - ^2D$	$3\sqrt{3}$ $3(15/2)^{1/2}$ $-3(15/2)^{1/2}$	$\sigma_1 + 10\sigma_2$ $\sigma_1 + 7\sigma_2$ $\sigma_1 + \sigma_2$
7	2	3	$^4S - ^4P$ $^2D - ^2D$ $^2D - ^2P$	$3\sqrt{3}$ $-3(15/2)^{1/2}$ $-3(15/2)^{1/2}$	$\sigma_1 + \sigma_3$ $\sigma_1 + \sigma_3 + 3\sigma_2$ $\sigma_1 + \sigma_3 + 9\sigma_2$
8	2	4	$^3P - ^3P$ $^1D - ^1P$	$-3\sqrt{6}$ $3\sqrt{10}$	$\sigma_1 + \sigma_3 + 5\sigma_2$ $\sigma_1 + \sigma_3 + 11\sigma_2$
9	2	5	$^2P - ^2S$	$-3\sqrt{3}$	$\sigma_1 + \sigma_3 + 10\sigma_2$

matrix elements:

$$\begin{aligned} \langle \Psi(\Gamma LS|N) || \bar{Q}_\lambda(N) || \Psi(\Gamma' L' S' |N) \rangle &= \langle \Psi_0(\Gamma LS|N) || \bar{Q}_\lambda(N) || \Psi_0(\Gamma' L' S' |N) \rangle \\ &+ (1/Z) [\langle \Psi_0(\Gamma LS|N) || \bar{Q}_\lambda(N) || \Psi_1(\Gamma' L' S' |N) \rangle \\ &+ \langle \Psi_1(\Gamma LS|N) || \bar{Q}_\lambda(N) || \Psi_0(\Gamma' L' S' |N) \rangle] + \dots \\ &= I_0 + (1/Z) I_1 + \dots \end{aligned}$$

We have, by Eq. (1),

$$\begin{aligned} I_0 &= \langle \Psi_0(\Gamma LS|N) || \bar{Q}_\lambda(N) || \Psi_0(\Gamma' L' S' |N) \rangle \\ &= \frac{N}{2} \sum_{\Gamma_1 L_1 S_1} \sum_{\Gamma_2 L_2 S_2} \sum_{\Gamma'_1 L'_1 S'_1} \sum_{\Gamma'_2 L'_2 S'_2} (\Gamma_1 L_1 S_1, \Gamma_2 L_2 S_2 | \Gamma LS) (\Gamma'_1 L'_1 S'_1, \Gamma'_2 L'_2 S'_2 | \Gamma' L' S') \\ &\quad \times \langle \{ \Psi_0(\Gamma_1 L_1 S_1 | 2), \psi_0(\Gamma_2 L_2 S_2 | N-2) \} || \bar{Q}_\lambda(2) || \{ \Psi_0(\Gamma'_1 L'_1 S'_1 | 2), \Psi_0(\Gamma'_2 L'_2 S'_2 | N-2) \} \rangle, \end{aligned}$$

which can be simplified to

$$\begin{aligned} I_0 &= \frac{N}{2} [(2L+1)(2L'+1)]^{1/2} \sum_{\Gamma_1 L_1 S_1} \sum_{\Gamma_2 L_2 S_2} \sum_{\Gamma'_1 L'_1 S'_1} (-1)^{L_1+\lambda+L_2+L'} \left\{ \begin{matrix} L_2 & L_1 & L \\ \lambda & L' & L'_1 \end{matrix} \right\} (\Gamma_1 L_1 S_1, \Gamma_2 L_2 S_2 | \Gamma LS) \\ &\quad \times (\Gamma'_1 L'_1 S'_1, \Gamma_2 L_2 S_2 | \Gamma' L' S') \langle \Psi_0(\Gamma_1 L_1 S_1 | 2) || \bar{Q}_\lambda(2) || \Psi_0(\Gamma'_1 L'_1 S'_1 | 2) \rangle \delta_{\Gamma_2 \Gamma'_2} \delta_{L_2 L'_2} \delta_{S_2 S'_2}, \quad (3) \end{aligned}$$

where $\left\{ \begin{matrix} L_2 & L_1 & L \\ \lambda & L' & L'_1 \end{matrix} \right\}$ is a Wigner 6- j symbol.¹⁰

Invoking the orthogonality of $\Psi(\Gamma LS|N)$ and $\Psi(\Gamma' L' S' |N)$, we similarly find

$$\begin{aligned} I_1 &= \langle \Psi_0(\Gamma LS|N) || \bar{Q}_\lambda(N) || \Psi_1(\Gamma' L' S' |N) \rangle + \langle \Psi_1(\Gamma LS|N) || \bar{Q}_\lambda(N) || \Psi_0(\Gamma' L' S' |N) \rangle \\ &= \frac{N(N-1)}{2} [(2L+1)(2L'+1)]^{1/2} \sum_{\Gamma_1 L_1 S_1} \sum_{\Gamma_2 L_2 S_2} \sum_{\Gamma'_1 L'_1 S'_1} (-1)^{L_1+\lambda+L_2+L'} \left\{ \begin{matrix} L_2 & L_1 & L \\ \lambda & L' & L'_1 \end{matrix} \right\} (\Gamma_1 L_1 S_1, \Gamma_2 L_2 S_2 | \Gamma LS) \\ &\quad \times (\Gamma'_1 L'_1 S'_1, \Gamma_2 L_2 S_2 | \Gamma' L' S') [\langle \Psi_0(\Gamma_1 L_1 S_1 | 2) || \bar{Q}_\lambda(2) || \Psi_1(\Gamma'_1 L'_1 S'_1 | 2) \rangle + \langle \Psi_1(\Gamma_1 L_1 S_1 | 2) || \bar{Q}_\lambda(2) || \Psi_0(\Gamma'_1 L'_1 S'_1 | 2) \rangle] \\ &\quad \times \delta_{\Gamma_2 \Gamma'_2} \delta_{L_2 L'_2} \delta_{S_2 S'_2}, \quad (4) \end{aligned}$$

where, by the Wigner-Eckart theorem,¹⁰ the reduced-matrix elements are given by

$$\langle \Psi(\Gamma_1 L_1 S_1 M_{L_1} M_{S_1} | 2) | Q_{\lambda K}(2) | \Psi(\Gamma'_1 L'_1 S'_1 M_{L'_1} M_{S'_1} | 2) \rangle = (-1)^{L_1 - M_{L_1}} \begin{pmatrix} L_1 & \lambda & L'_1 \\ -M_{L_1} & K & M_{L'_1} \end{pmatrix} \langle \Psi(\Gamma_1 L_1 S_1 | 2) || \bar{Q}_\lambda(2) || \Psi(\Gamma'_1 L'_1 S'_1 | 2) \rangle,$$

TABLE III. Transition probabilities for $1s^2 2s 2p \ ^3P - 1s^2 2p^2 \ ^3P$ transitions in the beryllium isoelectronic sequence, in units of 10^8 sec^{-1} .

Z	λ (Å)	Present calculation	Other calculations	Experiment
4	2650.6	4.185	4.3 ^a	4.13 ± 0.12, ^b 4.2 ± 0.2, ^c 4.3 ± 0.4 ^d
5	1624.0	8.51	8.4, ^e 8.8 ^a	7.3 ± 0.5, ^f 8.0 ± 0.4, ^g 7.7 ± 0.4, ^c 10.0 ± 2.0 ^h
6	1175.7	12.95	13.3, ^e 14.3 ⁱ	12.7 ± 0.4, ^j 12.5 ± 0.6, ^k 13.5 ± 1.4, ^l 10.8 ± 2.0 ^m
7	923.15	17.39	18.8 ⁱ	14.3 ± 1.1, ⁿ 15.3 ± 1.5, ^l 15.4 ± 2.3 ^o
8	760.36	21.84	23.3, ⁱ 22.38 ^a	21.7 ± 2.2 ^p
10	561.59	30.90	32.5 ⁱ	

^a Reference 20.

^b Reference 26.

^c Reference 31.

^d Reference 32.

^e Reference 21.

^f Reference 22.

^g Reference 23.

^h Reference 33.

ⁱ Reference 25.

^j Reference 22.

^k Reference 27.

^l Reference 29.

^m Reference 30.

ⁿ Reference 28.

^o Reference 56.

^p Reference 34.

TABLE IV. Transition probabilities for $1s^2 2s 2p \ ^1P - 1s^2 2p^2 \ ^1D$ transitions in the beryllium isoelectronic sequence, in units of 10^8 sec^{-1} .

Z	λ (Å)	Present calculation	Other calculations	Experiment
5	3451.4	0.77	0.50, ^a 0.54 ^b	0.64 ± 0.03 , ^c 0.78 ± 0.06 , ^d 0.72 ± 0.04 , ^e 0.63 ± 0.02 ^f
6	2296.9	1.56	1.57, ^g 1.25, ^a 1.38 ^b	1.35 ± 0.11 , ^h 1.4 ± 0.04 , ⁱ 1.4 , ^j 1.4 , ^k 1.08 ± 0.05 , ^c 1.33 ± 0.05 , ^l 1.23 ± 0.06 , ^m 1.10 ± 0.04 , ^f 1.39 ± 0.28 , ⁿ
7	1718.5	2.47	2.57, ^g 2.32, ^a 2.17 ^b	3.2 ± 0.2 , ^o 2.1 ^k
8	1371.3	3.46	3.62, ^b 3.31 ^a	3.3 ± 0.1 , ^p 3.1, ^k 3.2, ^q 3.1 ± 0.2 , ^r 3.4 ± 0.2 , ^s 3.1 ± 0.3 ^t
9	1139.5	4.51	4.50 ^a	4.35 ± 0.20 ^p
10	973.6	5.61	6.73, ^g 5.5 ^u	4.95 ± 0.2 ^v

^a Reference 35.

^b Reference 20.

^c Reference 26.

^d Reference 40.

^e Reference 32.

^f Reference 31.

^g Reference 25.

^h Reference 38.

ⁱ Reference 39.

^j Reference 41.

^k Reference 42.

^l Reference 37.

^m Reference 43.

ⁿ Reference 30.

^o Reference 44.

^p Reference 45.

^q Reference 46.

^r Reference 34.

^s Reference 47.

^t Reference 53.

^u Reference 18.

^v Reference 36.

considering \bar{Q}_λ to be a spin-independent operator.

The reduced-matrix elements in Eq. (3) can easily be evaluated directly. Those in Eq. (4) can be evaluated exactly, in the absence of zero-order mixing, by use of an interchange theorem. When \bar{Q}_λ is the electric dipole transition operator, $\bar{Q}_i = \sum_{i=1}^N \vec{r}_i$, and only $2s-2p$ transitions are considered, the calculations are rather straightforward. The necessary reduced-matrix elements are given in Table I.

Although the above analysis can be applied to calculate matrix elements correct to first order for a general N -electron atom, we here restrict our attention to $2s-2p$ dipole transitions in second-row atoms. The required coefficients of fractional percentage have been tabulated by Chisholm, Dalgarno, and Innes.¹¹

III. ZERO-ORDER MIXING

The analysis has to be modified when zero-order mixing occurs. Suppose the zero-order eigenfunction $\Psi_0(\Gamma LS|N)$ is s -fold degenerate so that there are s eigenfunctions $\Psi_0^{(k)}(\Gamma LS|N)$, $k=1, \dots, s$, corresponding to the eigenvalue $E_0(\Gamma LS|N)$. We choose the $\Psi_0^{(k)}$ to diagonalize H ,

$$\langle \Psi_0^{(k)} | H | \Psi_0^{(k')} \rangle = (E_0 + E_1^{(k)}) \delta_{kk'},$$

so that the $\Psi_1^{(k)}$, $k=1, \dots, s$, satisfy Eq. (2). However, unlike the nondegenerate case, Eq. (2) does not define $\Psi_1^{(k)}$ uniquely: the solutions of (2) are arbitrary with respect to the addition of arbitrary multiples of $\Psi_0^{(k')}$, $k'=1, \dots, s$.

Define

TABLE V. Transition probabilities for $1s^2 2s 2p^2 \ ^4P - 1s^2 2p^3 \ ^4S$ transitions in the boron isoelectronic sequence, in units of 10^8 sec^{-1} .

Z	λ (Å)	Present calculation	Other calculations	Experiment
5	1466.0	19.64	19.8 ^a	16.0 ± 1.0 ^b
6	1010.2	33.61	34.3 ^a	33.0 ± 1.0 , ^c 32.0 ± 3.0 ^d
7	772.1	48.05	49.0, ^a 57.4 ^e	
8	625.4	62.68	64.0, ^a 72.8 ^e	52.6 ± 8.0 ^f
9	526.3	77.17	78.7 ^a	
10	453.3	92.41	93.5 ^a	

^a Reference 48.

^b Reference 22.

^c Reference 27.

^d Reference 29.

^e Reference 57.

^f Reference 34.

TABLE VI. Transition probabilities for $1s^2 2s 2p^2 2P-1s^2 2p^3 2D$ transitions in the boron isoelectronic sequence, in units of 10^8 sec^{-1} .

Z	λ (Å)	Present calculation	Other calculations	Experiment
6	2511.0	0.93	0.64 ^a	0.86, ^b 0.89 ± 0.22 ^c
7	1750.4	1.81	1.48, ^d 2.6 ^e	1.5 ^f
8	1343.0	2.83	2.51, ^d 3.8 ^e	
9	1087.8	3.97	3.69 ^d	
10	927.0	4.96	4.80 ^d	

^a Reference 49.

^b Reference 50.

^c Reference 63.

^d Reference 48.

^e Reference 57.

^f Reference 64.

$$\chi_1^{(k)} = \sum_j' \frac{\langle \Psi_0^{(k)} | H_1 | \Psi_0^{(j)} \rangle}{E_0 - E_0^{(j)}} \Psi_0^{(j)}, \quad k=1, \dots, s,$$

where the prime on the summation means that $j \neq k$, $k=1, \dots, s$, and $\Psi_0^{(j)}$ is an eigenfunction of H_0 with eigenvalue $E_0^{(j)}$. $\chi_1^{(k)}$ is thus a solution of Eq. (2) with $\langle \chi_1^{(k)} | \Psi_0^{(k')} \rangle = 0$, $k'=1, \dots, s$. The most general solution of (2) can now be written as

$$\Psi_1^{(k)} = \chi_1^{(k)} + \sum_{k'=1}^s b_{kk'} \Psi_0^{(k')},$$

where the $b_{kk'}$, which are not at our disposal, are determined from the second-order equation

$$(H_0 - E_0) \Psi_2^{(k)} + (H_1 - E_1^{(k)}) \Psi_1^{(k)} = E_2^{(k)} \Psi_0^{(k)}.$$

Thus

$$b_{kk'} = \frac{\langle \Psi_0^{(k')} | H_1 | \chi_1^{(k)} \rangle}{E_1^{(k)} - E_1^{(k')}}, \quad k \neq k'$$

$$= 0, \quad k = k'.$$

It is clear from the definition of $b_{kk'}$ that

$$b_{kk'} + b_{k'k} = 0.$$

The result also follows from the requirement that $\langle \Psi^{(k)} | \Psi^{(k')} \rangle = \delta_{kk'}$, through first order.

In the analysis we have assumed that the degeneracy is lifted in first order, which is, of course, the case for $2s^2-2p^2$ degeneracies. More-detailed studies of the degeneracy problem in Rayleigh-Schrödinger perturbation theory have been performed by Hirschfelder¹² and by Silverstone,¹³ who considered the general case in which degeneracy is first removed in the n th order.

It is interesting to note that the quantities $b_{kk'}$ do not affect the second- and third-order energies; for example,

$$E_2^{(k)} = \langle \Psi_0^{(k)} | H_1 - E_1^{(k)} | \Psi_1^{(k)} \rangle$$

$$= \langle \Psi_0^{(k)} | H_1 - E_1^{(k)} | \chi_1^{(k)} \rangle,$$

which clearly does not depend on $b_{kk'}$. This is generally not the case for matrix elements of operators other than H : through first order the result will involve the $b_{kk'}$. In particular, if $\Psi_0^{(i)} (\Gamma L S | N)$ is s -fold degenerate, then, through

TABLE VII. Transition probabilities for $1s^2 2s 2p^2 2D-1s^2 2p^3 2D$ transitions in the boron isoelectronic sequence, in units of 10^8 sec^{-1} .

Z	λ (Å)	Present calculation	Other calculations	Experiment
6	1323.9	7.06	5.25 ^a	5.4 ± 0.5 ^b
7	979.9	11.23	9.52, ^c 4.8 ^d	10.0 ± 5.0 , ^e 12.4 ± 1.2 ^b
8	779.8	15.57	14.15, ^c 19.5 ^d	
9	647.8	20.03	19.07 ^c	
10	557.0 ^c	24.20	23.86 ^c	

^a Reference 49.

^b Reference 29.

^c Reference 57.

^d Reference 57.

^e Reference 58.

TABLE VIII. Transition probabilities for $1s^2 2s^2 2p^3 4S-1s^2 2s 2p^4 4P$ transition in the nitrogen isoelectronic sequence, in units of 10^8 sec^{-1} .

Z	λ (Å)	Present calculation	Other calculations	Experiment
7	1134.6	4.82	8.44, ^a 18.1, ^b 2.8, ^f 8.13 ^g	1.45±0.04, ^c 1.39±0.1, ^d 2.3 ^e 2.25±0.45, ^h 1.0±0.1, ⁱ 1.35±0.07 ^j
8	833.8	8.49	6.9, ^f 13.7 ^a	8.0±0.6 ^k
9	658.3	12.72		
10	542.8	17.43		15.0±0.5 ^l

^a Reference 57. ^d Reference 33. ^g Reference 49. ^j Reference 60.
^b Reference 54. ^e Reference 52. ^h Reference 59. ^k Reference 61.
^c Reference 51. ^f Reference 55. ⁱ Reference 58. ^l Reference 62.

first order,

$$\begin{aligned} \langle \Psi^{(i)}(\Gamma L S | N) || \tilde{Q}_\lambda(N) || \Psi(\Gamma' L' S' | N) \rangle \\ = \langle \Psi_0^{(i)}(\Gamma L S | N) || \tilde{Q}_\lambda(N) || \Psi_0(\Gamma' L' S' | N) \rangle + (1/Z) [\langle \Psi_0^{(i)}(\Gamma L S | N) || \tilde{Q}_\lambda(N) || \Psi_1(\Gamma' L' S' | N) \rangle \\ + \langle \chi_1^{(i)}(\Gamma L S | N) || \tilde{Q}_\lambda(N) || \Psi_0(\Gamma' L' S' | N) \rangle + \sum_{i'=1}^s b_{ii'} \langle \Psi_0^{(i')}(\Gamma L S | N) || \tilde{Q}_\lambda(N) || \Psi_0(\Gamma' L' S' | N) \rangle]. \end{aligned}$$

It has been noted by Hirschfelder, Brown, and Epstein¹⁴ that $b_{ii'}$ cannot be calculated by the use of an interchange theorem. Thus, whereas $\langle \Psi_0^{(i)} || \tilde{Q}_\lambda(N) || \Psi_1 \rangle$ and $\langle \chi_1^{(i)} || \tilde{Q}_\lambda(N) || \Psi_0 \rangle$ can be evaluated exactly, $b_{ii'}$ requires explicit knowledge of the first-order wave functions, and can therefore only be evaluated approximately.

IV. TRANSITION PROBABILITIES

The probability of an electric dipole transition from an upper level $\Gamma L S$ with statistical weight g to a lower level $\Gamma' L' S'$ is given, in terms of the absolute multiplet strength $S(\Gamma L S, \Gamma' L' S')$, by

$$A = \frac{2.026 \times 10^{18}}{\lambda^3 g} S(\Gamma L S, \Gamma' L' S') \text{ sec}^{-1},$$

TABLE IX. Transition probabilities for $1s^2 2s^2 2p^3 2D-1s^2 2s 2p^4 2P$ transitions in the nitrogen isoelectronic sequence, in units of 10^8 sec^{-1} .

Z	λ (Å)	Present calculation	Other calculations	Experiment
8	718.5	20.7	19.8, ^a 34.0 ^b	23.0±2.5 ^c
9	567.7	30.7		
10	469.8	41.5		

^a Reference 55.
^b Reference 57.
^c Reference 61.

where λ is the wavelength, in angstroms, of the photons emitted in the transition and $S(\Gamma L S, \Gamma' L' S')$ is defined by

$$S(\Gamma L S, \Gamma' L' S') = (2S+1) |\langle \Psi(\Gamma L S | N) || \tilde{Q} || \Psi(\Gamma' L' S' | N) \rangle|^2, \quad (5)$$

with

$$\tilde{Q} = \sum_{i=1}^N r_i.$$

Using our Z expansion of the reduced-matrix element on the right-hand side of Eq. (5) and the screening approximation of Dalgarno and Stewart,¹⁵ we can write

$$\begin{aligned} S(\Gamma L S, \Gamma' L' S') &= (2S+1) |I_0/Z + I_1/Z^2 + \dots|^2 \\ &= (2S+1) \left(\frac{I_0}{Z-\sigma} \right)^2, \quad \sigma = I_1/I_0. \quad (6) \end{aligned}$$

The values of I_0 and σ for the transitions consid-

TABLE X. Transition probabilities for $1s^2 2s^2 2p^3 2D-1s^2 2s 2p^4 2P$ transitions in the nitrogen isoelectronic sequence, in units of 10^8 sec^{-1} .

Z	λ (Å)	Present calculation
8	538.3	88.6
9	430.2	125.9
10	358.4	165.1

TABLE XI. Radiative lifetimes of $1s^2 2p^3 2D$ states of boronlike ions, in units of 10^{-9} sec.

System	Present calculation	Weiss (Refs. 48 and 49)	Experiment
CII	1.25	1.7	2.5 ± 0.1 , ^a 1.8 , ^b 2.1 ± 0.2 ^c 1.85 ± 0.2 , ^d 2.0 ± 0.4 , ^e 1.83 ± 0.18 ^f
NIII	0.77	0.9	0.97 ± 0.3 , ^g 1.04 ± 0.04 , ^h 0.80 ± 0.12 , ⁱ 1.0 ± 0.5 ^j
OIV	0.54	0.6	0.53 ± 0.14 , ^k 0.65 ± 0.07 , ^l 0.9 ^{m,n}
NeVI	0.34	0.35	

^a Reference 43.^b Reference 41.^c Reference 26.^d Reference 65.^e Reference 30.^f Reference 29.^g Reference 51.^h Reference 64.ⁱ Reference 56.^j Reference 58.^k Reference 47.^l Reference 34.^m Reference 46.ⁿ Reference 66.

ered in this paper are presented in Table II.

If $\Gamma'L'S$ is the only level to which the level ΓLS can decay by emission of electric dipole radiation, then the mean lifetime of the upper level is $\tau = A^{-1}$ sec. Beam-foil spectroscopy has been widely used by many workers to measure the lifetimes of excited states of atomic ions and so, in many cases, we can make direct comparison with the experimental results. We use experimental energy differences^{16,21} and tabulate results for a range of ions in Tables III-X, including, where possible, experimental measurements and other calculated values for comparison.

Several general conclusions can immediately be drawn from Tables III-X. As expected, the agreement between our Z -expansion results and the results of other accurate calculations and experimental data improves with increasing degrees of ionization. The $2s2p^1P^o - 2p^2^1D$ transition in berylliumlike ions is a good illustration, where the transition probabilities predicted by the Z -expansion¹⁷ method differ by less than 5% from the

nonclosed shell many-electron-theory results of Nicolaidis, Beck, and Sinanoglu¹⁸ for OV, FVI, and NeVII. Thus after a few stages of ionization, elaborate calculations are usually unnecessary to obtain accurate values for oscillator strengths and transition probabilities, the relatively simple method of prediction afforded by the Z -expansion scheme being entirely adequate. The accuracy of Z -expansion results near the neutral end of the isoelectronic sequence is often very good, due partly to the screening approximation (6), which works well for transitions in which there is no change of principal quantum number.

The experimentally determined transition probabilities are invariably smaller than our theoretical values. In the measurement of the radiative lifetime of an excited ionic level by the beam foil technique the level is populated not only by excitations in the foil, but also by cascading from higher levels. The theoretical results suggest that cascading effects may be more important than has been assumed.¹⁹

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Symmetry of a Hydrogen Atom in a Weak Magnetic Field

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The degeneracy problem of a hydrogen atom in a uniform weak magnetic field H is considered from the standpoint of the invariance group that the system obeys. Evidently the degeneracy space has a constant z component of the angular momentum. Under such a classification, the dynamical invariance of the problem is shown to be an isomorph to the Lie group of the linear transformation of the straight line.

I. INTRODUCTION AND THEORY

The degeneracy problem of a hydrogen atom in a uniform magnetic field seems to be interesting in the field of dynamical symmetry. When the field strength H tends toward negligibly small values and the Coulomb term becomes predominant, the invariance group for the system is just the one which the hydrogen atom obeys. This de-

generacy has long been discussed since the Runge-Lenz vector^{1,2} was discovered, and has been reviewed elsewhere in the textbooks.^{3,4} This invariance group, as is well known, is $O(4)$. In the opposite limit, on the contrary, the Hamiltonian of a free electron moving in a uniform magnetic field has an invariance group $G(0,1)$, as pointed out by the authors previously.^{5,6}

In this paper the first approach to the intermedi-