Polarizability of Mg+2 Derived from Hydrogen-Like Terms of Mg II

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It is shown that the two series $ng\ ^2G(n=5-11)$ and $nh\ ^2H(n=7-10)$ of Mg II, which were recently determined with great accuracy by Risberg, can be represented within the experimental errors by the polarization formula for nonpenetrating orbits, which contains as single adjustable parameter the polarizability α of the atom core. The value of α thus obtained for Mg+2 is $(0.0720\pm0.0010)\times10^{-24}$ cm^3.

IN a study of the term system of C IV, it was found desirable to calculate the values of certain hydrogen-like terms by using the polarization formula for non-penetrating orbits. To get an estimate of the obtainable accuracy, the formula was first applied to Mg II, which, after the recent observations by Risberg,[1] offers by far the best material for such a test. The following note gives the results obtained for Mg II.

Bohr[2] was the first to point out that the polarization of the atom core in the field of the valence electron will produce a quantum defect for nonpenetrating orbits in alkali-like spectra. Born and Heisenberg[3] treated this effect on the basis of the old quantum theory, and Waller[4] gave the quantum-mechanical theory.

Waller obtains from the perturbation theory a relation that can be written

$$RZ_0^2/(n^*)^2 = RZ_0^2/n^2 + R\alpha a_0\langle r^{-4}\rangle, \qquad (1)$$

where R is the Rydberg constant, Z_0 the net charge of the core, n the principal quantum number, n^* the effective principal quantum number, α the polarizability of the core, a_0 the radius of the first Bohr orbit of hydrogen, and $\langle r^{-4}\rangle$ the average of r^{-4} taken over the unperturbed system, r being the distance from the nucleus to the valence electron. For this average, Waller derived the expression

$$\langle r^{-4}\rangle = \frac{Z_0^4[3n^2-l(l+1)]}{2a_0^4n^5(l-\tfrac{1}{2})l(l+\tfrac{1}{2})(l+1)(l+\tfrac{3}{2})}, \qquad (2)$$

where l is the azimuthal quantum number. Introducing

the term value $T = RZ_0^2/(n^*)^2$, the corresponding hydrogenic term value $T_0 = RZ_0^2/n^2$, and the expression (2) in Eq. (1), one obtains

$$T = T_0 + C\frac{3n^2-l(l+1)}{n^5(l-\tfrac{1}{2})l(l+\tfrac{1}{2})(l+1)(l+\tfrac{3}{2})}, \qquad (3)$$

where $C = \alpha RZ_0^4/2a_0^3$. The term values are thus given in terms of the quantum numbers n and l and the parameter α.

A calculation of α based on spectroscopic term values has been made for several ions with rare gas structure by Mayer and Mayer.[5] They derive and apply corrections for the effect of penetration and for quadrupole polarization of the ion.

The quadrupole polarization can be accounted for by adding a term proportional to $\langle r^{-6}\rangle$, writing

$$C = C_0(1 + k\langle r^{-6}\rangle/\langle r^{-4}\rangle), \qquad (4)$$

where k is constant for a given ion. C/C_0 has been calculated for several ions by Mayer and Mayer and by Sternheimer.[6] The k-values from Sternheimer's calculation are on the average about twice as large as those found by Mayer and Mayer. He did not treat the Mg+2 ion, however.

The quantum-mechanical value of $\langle r^{-6}\rangle$ has been calculated by Van Vleck[7] and given in terms of certain parameters, which are in turn expressed in the quantum numbers n and l. If one replaces the parameters by these expressions, the value can be given explicitly in terms of n and l:

$$\langle r^{-6}\rangle = \frac{Z_0^6\{35n^4-5n^2[6l(l+1)-5]+3(l-1)l(l+1)(l+2)\}}{8a_0^6n^7(l-\tfrac{3}{2})(l-1)(l-\tfrac{1}{2})l(l+\tfrac{1}{2})(l+1)(l+\tfrac{3}{2})(l+2)(l+5/2)}. \qquad (5)$$

The quotient $\langle r^{-6}\rangle/\langle r^{-4}\rangle$ is seen to approach the value $35Z_0^2/[12a_0^2(l-\tfrac{3}{2})(l-1)(l+2)(l+5/2)]$ for large values of n.

When applying formula (3) to Mg II, the constant C has been determined from the first five members of the ^2G series by the method of least squares, giving $C = 429\ 900$ cm^{-1}. Inserting this value of C and the

appropriate values of l in Eq. (3), one gets the formulas

$$ng\ ^2G:\quad T = T_0 + 248.14(3n^2-20)/n^5, \qquad (6)$$

$$nh\ ^2H:\quad T = T_0 + 267.23(n^2-10)/n^5, \qquad (7)$$

with

$$T_0 = 438\ 939.33/n^2. \qquad (8)$$

[1] P. Risberg, Arkiv Fysik 9, 483 (1955).
[2] N. Bohr, Ann. Physik [4] 71, 262 (1923).
[3] M. Born and W. Heisenberg, Z. Physik 23, 388 (1924).
[4] I. Waller, Z. Physik 38, 635 (1926).

[5] J. E. Mayer and M. Goeppert-Mayer, Phys. Rev. 43, 605 (1933).
[6] R. M. Sternheimer, Phys. Rev. 96, 951 (1954).
[7] J. H. Van Vleck, Proc. Roy. Soc. (London) A143, 679 (1934).

TABLE I. $ng\,^2G$ terms of Mg II.

n	T_{obs}, cm^{-1}	T_0, cm^{-1}	$T_{obs}-T_0$	$T_{calc}-T_0$	$T_{obs}-T_{calc}$
5	17 561.946	17 557.573	4.373	4.367	+0.006
6	12 195.561	12 192.759	2.802	2.808	−0.006
7	8959.821	8957.946	1.875	1.875	0.000
8	6859.725	6858.427	1.298	1.302	−0.004
9	5419.937	5419.004	0.933	0.937	−0.004
10	4390.071	4389.393	0.678	0.695	−0.017
11	3628.097	3627.598	0.499	0.528	−0.029

TABLE II. $nh\,^2H$ terms of Mg II.

n	T_{obs}, cm^{-1}	T_0, cm^{-1}	$T_{obs}-T_0$	$T_{calc}-T_0$	$T_{obs}-T_{calc}$
6	⋯	12 192.759	⋯	0.894	⋯
7	8958.552	8957.946	0.606	0.620	−0.014
8	6858.868	6858.427	0.441	0.440	+0.001
9	5419.329	5419.004	0.325	0.321	+0.004
10	4389.574	4389.393	0.181	0.241	−0.060

In Tables I and II are listed the term values, T_{obs}, as observed by Risberg, the hydrogenic term values, T_0, the differences $T_{obs}-T_0$, the differences $T_{calc}-T_0$ obtained from (6) or (7), and the residuals $T_{obs}-T_{calc}$. Risberg gives the term values with two decimals and has estimated their limits of error to be about 0.02 cm^{-1} on the average. With his permission the values are given here with three decimals, taken from his working list, to facilitate a comparison with the calculated values.

The tables show that the ^2G and the ^2H series are indeed represented within the experimental errors by the polarization formula with the single adjustable parameter α. The deviation for the last member of each series also appears when the series are represented by Ritz formulas.

The ^2F series cannot be accurately represented by the simple polarization formula for any value of α. In Table III, $T_{calc}-T_0$ have been calculated from the formula

$$T=T_0+2729.5(n^2-4)/n^5, \qquad (9)$$

which is obtained from (3) by using the same value of C as before. $T_{obs}-T_{calc}$ gives the quantity that cannot be explained by the simple formula and which must be due to penetration and to polarization of higher order.[8]

The value of C obtained from the ^2G series gives $\alpha=0.0726\times10^{-24}$ cm^3. The uncertainty of the observed term values gives a maximum error in α of 0.0004×10^{-24}. If some part of the term defect, $T_{obs}-T_0$, is due to the effect of penetration or higher order polarization, the

[8] *Note added in proof.*—The ^2F series can in fact be accurately described by means of a two-parameter formula, obtained by combining Eqs. (3) and (4), which indicates that the deviation is largely due to quadrupole polarization. [K. Bockasten, Arkiv Fysik (to be published).]

value of α will be correspondingly smaller. Table IV gives the values of $\langle r^{-6}\rangle/\langle r^{-4}\rangle$ in terms of Z_0^2/a_0^2 for the ^2F, ^2G, and ^2H series. The values of C/C_0 given by Mayer and Mayer $(=C_q$ in their notation) correspond to $kZ_0^2/a_0^2=1.237$. If their estimates of C_q are correct, the value of α will then be reduced to 0.0720×10^{-24}.

An investigation of Table I of Mayer and Mayer shows that for the ions contained in the table the calculated change in term value due to penetration is generally smaller than the change due to quadrupole polarization. If, therefore, the value of α is given as $(0.0720\pm0.0010)\times10^{-24}$ cm^3, the limits will allow for a possible penetration effect as large as the effect of the quadrupole polarization.

This value may be compared to the results of Mayer and Mayer. From the first three terms of the ^2D series

TABLE III. $nf\,^2F$ terms of Mg II.

n	T_{obs}, cm^{-1}	T_0, cm^{-1}	$T_{obs}-T_0$	$T_{calc}-T_0$	$T_{obs}-T_{calc}$
4	27 467.91	27 433.71	34.20	31.99	2.21
5	17 577.72	17 557.57	20.15	18.34	1.81
6	12 205.27	12 192.76	12.51	11.23	1.28
7	8966.14	8957.95	8.19	7.31	0.88
8	6864.06	6858.43	5.63	5.00	0.63
9	5423.01	5419.00	4.01	3.56	0.45
10	4392.36	4389.39	2.97	2.62	0.35

TABLE IV. Values of $(\langle r^{-6}\rangle/\langle r^{-4}\rangle)\times(a_0^2/Z_0^2)$.

n	$nf\,^2F$	$ng\,^2G$	$nh\,^2H$
4	0.0208	⋯	⋯
5	0.0267	0.0053	⋯
6	0.0295	0.0069	0.0020
7	0.0311	0.0078	0.0026
8	0.0322	0.0084	0.0029
9	0.0329	0.0087	0.0032
∞	0.0354	0.0100	0.0040

of Mg II they obtained the polarizability 0.105, 0.107, and 0.107×10^{-24} and from the first three terms of the ^2F series 0.072, 0.074, and 0.072×10^{-24}. As the most probable value, they give 0.10×10^{-24}. Their values from the ^2F terms are in good agreement with the present results. Comparison can also be made with the value 0.094×10^{-24} derived from the atomic refraction of Mg^{+2} as calculated by Pauling.[9]

[9] L. Pauling, Proc. Roy. Soc. (London) **A114**, 181 (1927).