

The Interaction of Configurations: $sd - p^2$

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It does not seem possible to account for the presence of singlets below their triplets in two electron spectra simply from the ordinary exchange integrals. The exchange integrals seem to be essentially positive. It is shown that the matrix component of electrostatic energy connecting

the $3s3d^1D$ with $3p^2^1D$ in Mg I is sufficiently large to account for the occurrence of $3s3d^1D$ below $3s3d^3D$ as observed experimentally. Analytic radial wave functions of the type developed by Slater are used in the calculation of the nondiagonal elements.

THE spectra of elements and ions which contain two valence electrons outside closed p or d shells, are in general quite regular. That is, the energy states are for the most part those for which one electron remains in a low s -state and the other takes on higher values of n and l . The resultant states are singlet and triplet terms with the L determined from the second electron. For some of the heavier elements which follow the completion of a d -shell there are many other terms which arise when one of the d -electrons is excited from its closed shell. The presence of these states causes large perturbations in the singlets and triplets, disturbing both their multiplet separations and their series. These perturbations are for the greater part quite complicated. If one considers only those cases for which only the two electrons are excited, the theory of Houston¹ is expected to hold. Condon and Shortley² have gathered together many examples of two electron spectra to see how they fit Houston's theory. The radial integrals which are involved in the theory are not calculated but are carried through as parameters for which certain relations are expected to hold from the theory. The radial integral of type (1) which gives the singlet-triplet separation is considered to be either positive (triplet below singlet) or negative (triplet above singlet). Condon and Shortley's work shows that for the cases for which the singlet is below the

triplet there is very poor agreement with the theory.

In studying these difficulties for the D terms of Mg I which is one of the simplest cases where the singlet lies below the triplet, it was found that with no reasonable radial functions for magnesium could the singlet ever be expected to come below the triplet. The singlet-triplet separation is given by the following expression:

$$\frac{1}{5} e^2 \int_0^\infty dr_1 R(3s, r_1) R(3d, r_1) \int_0^\infty dr_2 \frac{r_a^2}{r_b^3} R(3s, r_2) R(3d, r_2), \quad (1)$$

where $R(3s)$ and $R(3d)$ are one electron wave functions multiplied by r , and r_a is the smaller of r_1 and r_2 , and r_b the larger. Fig. 1 gives a plot of these two wave functions as determined by the method of Slater. The negative contribution to the first integral arises from the second maximum of the $3s$ which has the opposite sign from the $3d$ wave function. This part is quite small; in fact one may get a good first approximation to the

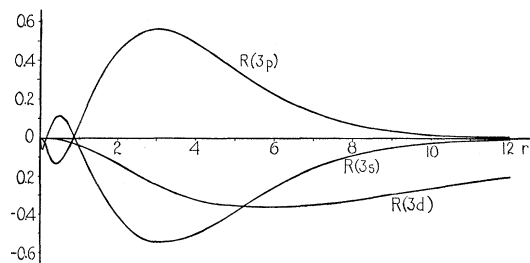


FIG. 1. $R(3p)$, $R(3s)$ and $R(3d)$ of Mg I as determined by the Slater method are plotted against r , where r is in units of the radius of the first Bohr orbit.

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¹ W. V. Houston, Phys. Rev. **33**, 297 (1929).

² E. U. Condon and G. H. Shortley, Phys. Rev. **35**, 1342 (1930).

integral by considering only the term in r^3 which gives the outer maximum of the $3s$ radial function. The same of course holds for the second integral. In other cases the first integral may be negative but then the second will be negative too and the product positive. This conclusion is a consequence of the position and relative magnitudes of the maxima of the radial wave functions and in general to get a negative integral would require very large and improbable distortions of the wave functions from hydrogen functions. It seems then that the examples of two-electron spectra for which the singlet lies below the triplet should not be expected to agree with the Houston theory and their explanation must lie elsewhere. It will be shown that perturbations by other configurations may be sufficiently large to account for them.

As pointed out by Condon,³ the interaction between configurations often becomes so large that it is necessary to consider both configurations together as one in calculating the various matrix components. Condon pointed out that this happens when two configurations of the same parity overlap. This interaction may also be very large under favorable circumstances even in case the configurations are well separated.

The lowest of the configurations arising when both of the valence electrons of two electron spectra are excited is the p^2 configuration, but it

seemed at first that it was quite unlikely that perturbations from this configuration could be causing the irregularity of the ordinary singlets and triplets, due to the fact that in some of the examples where the irregularity of the D terms is noted the p^2 levels are so much higher than this D level that they lie above the first ionization potential. Such an explanation seems to be the only one remaining, however, and this seems to be an indication that such interactions are very much larger in many cases than they have generally been supposed to be. The examples of the sd configuration which give the singlet below the triplet constitute the majority of such cases for two electron spectra, as would be expected if one considers that the even configuration p^2 lies very much lower than other configurations involving two excited electrons. This configuration does not perturb the sp and sf configurations because of the difference in parity and affects the ss configurations only in a lesser degree particularly in view of the larger "normal" triplet-singlet separation of the latter.

THE ENERGY MATRICES

If one includes both the electrostatic interaction and the spin-orbit interaction the Hamiltonian may be written as usual in the following form:

$$H = \sum_{\text{electrons}} \left[\frac{1}{2\mu} (p_x^2 + p_y^2 + p_z^2) - \frac{Ze^2}{r} + V(r)(l \cdot s) \right] + e^2 \sum_{\text{pairs } r_{12}} \frac{1}{r_{12}}$$

where the first sum is a sum of functions for each electron alone and the second for pairs of electrons. Since there are no components of H between states with different M_J it will be sufficient to consider only those of a single M_J value. In addition since, for Mg I and other simple cases the triplet is unaffected (the interval rule still holds), it will be sufficient to consider $M_J=2$, the largest value of M_J for which the singlet is represented and of course the simplest to treat. Furthermore after the transformation to $(L-S)$ wave functions the electrostatic energy in which we are particularly interested will have components only between states having the same L and S .

There are three states from the sd configuration and two from the p^2 included in the group $M_J=2$; ${}^3D_{3,2}$ 1D_2 and 3P_2 1D_2 , respectively. These five states have the m_s and m_l values for each electron and also resultant values for both electrons M_S and M_L as given in Table I. The diagonal and nondiagonal matrix compon-

TABLE I.

	s	d	M_S	M_L
1	$(\frac{1}{2}, 0)$	$(\frac{1}{2}, 1)$	1	1
2	$(-\frac{1}{2}, 0)$	$(\frac{3}{2}, 2)$	0	2
3	$(\frac{1}{2}, 0)$	$(-\frac{1}{2}, 2)$	0	2
4	$(\frac{1}{2}, 0)$	$(\frac{3}{2}, 1)$	1	1
5	$(-\frac{1}{2}, 1)$	$(\frac{1}{2}, 1)$	0	2
	p	p		

³ E. U. Condon, Phys. Rev. 36, 1121 (1930).

ents of H for these states are determined from expressions of the sort obtained by Condon³ and by Slater, in terms of wave functions built up as Slater⁴ did from one-electron wave functions. These will be referred to as the original wave functions. For convenience put $-Ze^2/r=H_1$; $V(r)(l \cdot s)=H_2$; and $e^2 1/r_{12}=H_3$. The matrix of H_3 has the following form in the original wave

TABLE II. Matrix of H_3 in original wave functions.

	1	2	3	4	5
1	$R_a - \frac{1}{5}R_b$	0	0	0	0
2	0	R_a	$-\frac{1}{5}R_b$	0	$(\frac{2}{15})^{\frac{1}{2}}R_c$
3	0	$-\frac{1}{5}R_b$	R_a	0	$(\frac{2}{15})^{\frac{1}{2}}R_c$
4	0	0	0	$R_d - \frac{1}{5}R_e$	0
5	0	$(\frac{2}{15})^{\frac{1}{2}}R_c$	$-(\frac{2}{15})^{\frac{1}{2}}R_c$	0	$R_d + \frac{1}{5}R_e$

functions (see Table II) where the R 's are various radial integrals.

$$R_a = R^0(3s, 3s; 3d, 3d); \quad R_b = R^2(3s, 3d; 3d, 3s)$$

$$R_c = R^1(3s, 3p; 3d, 3p); \quad R_d = R^0(3p, 3p; 3p, 3p)$$

$$R_e = R^2(3p, 3p; 3p, 3p),$$

where

$$R^k(\alpha, \beta; \gamma, \delta)$$

$$= e^2 \int_0^\infty dr_1 \int_0^\infty dr_2 R_\alpha(r_1) R_\gamma(r_1) \frac{r_1^k}{r_1^{k+1}} R_\beta(r_2) R_\delta(r_2).$$

H_1 has only diagonal components which are the same for all sd states and again for all p^2 states. H_2 , the magnetic interaction, has the form given in Table III. a and b are radial integrals depending on the form of $V(r)$. For the case of light

TABLE III. Matrix of H_2 in original wave functions.

	1	2	3	4	5
1	$\frac{1}{2}b$	0	b	0	0
2	0	b	0	0	0
3	b	0	$-b$	0	0
4	0	0	0	$\frac{1}{2}a$	$\frac{1}{2}a$
5	0	0	0	$\frac{1}{2}a$	0

⁴ J. C. Slater, Phys. Rev. **34**, 1293 (1929).

elements both a and b are sufficiently small to be neglected in comparison to the much larger terms in H_1 and H_2 .

In order to be able to assign L and S values to the various states it is useful to have these energy matrices in terms of $(L-S)$ wave functions. To do this, matrices for L^2 , S^2 and $L \cdot S$ are written down from the work of Johnson⁵ and the transformation to make all three diagonal is found in the same manner as his. The transformation matrix is given in Table IV. After the transfor-

TABLE IV. Transformation matrix.

	1	2	3	4	5
1	$(\frac{2}{3})^{\frac{1}{2}}$	$(\frac{1}{6})^{\frac{1}{2}}$	$(\frac{1}{6})^{\frac{1}{2}}$	0	0
2	$-(\frac{1}{3})^{\frac{1}{2}}$	$(\frac{1}{3})^{\frac{1}{2}}$	$(\frac{1}{3})^{\frac{1}{2}}$	0	0
3	0	$(\frac{1}{2})^{\frac{1}{2}}$	$-(\frac{1}{2})^{\frac{1}{2}}$	0	0
4	0	0	0	1	0
5	0	0	0	0	1

mation to $(L-S)$ wave functions H_3 and H_2 are given in Tables V and VI.

TABLE V. Matrix of H_3 in $(L-S)$ wave functions.

	3D_3	3D_2	1D_2	3P_2	1D_2
3D_3	$R_a - \frac{1}{5}R_b$	0	0	0	0
3D_2	0	$R_a - \frac{1}{5}R_b$	0	0	0
1D_2	0	0	$R_a + \frac{1}{5}R_b$	0	$2(\frac{1}{15})^{\frac{1}{2}}R_c$
3P_2	0	0	0	$R_d - \frac{1}{5}R_e$	0
1D_2	0	0	$2(\frac{1}{15})^{\frac{1}{2}}R_c$	0	$R_d + (\frac{1}{5})R_e$

TABLE VI. Matrix of H_2 in $(L-S)$ wave functions.

	3D_3	3D_2	1D_2	3P_2	1D_2
3D_3	b	0	0	0	0
3D_2	0	$-\frac{1}{2}b$	$(\frac{3}{2})^{\frac{1}{2}}b$	0	0
1D_2	0	$(\frac{3}{2})^{\frac{1}{2}}b$	0	0	0
3P_2	0	0	0	$\frac{1}{2}a$	$(\frac{1}{2})^{\frac{1}{2}}a$
1D_2	0	0	0	$(\frac{1}{2})^{\frac{1}{2}}a$	0

H_1 is, of course, still diagonal. The only non-diagonal matrix component in H_3 which now ap-

⁵ M. H. Johnson, Phys. Rev. **39**, 197 (1932).

pears is that between the two singlet D 's. H_3 , however, now contains several radial integrals which it is necessary to evaluate before going further. This may be simplified considerably in any particular case by calculating only those elements in which we are particularly interested and taking the rest from the experimental material. For example H_1 and the R_a and R_d terms of H_3 determine only the centers of gravity of the two electron configurations sd and p^2 and for the purpose of this work this may be taken from experimental material. There remain three radial integrals in H_3 and two in the magnetic interaction matrix. These last demand a knowledge of $V(r)$ for their evaluation and this function is known only very approximately. Fortunately for the cases of the lighter elements which compose many of the cases where the interaction between configurations may be simplified to the extent adopted here, the magnetic interactions are small compared to the electrostatic and may be neglected in first approximation.

THE RADIAL INTEGRALS

In order to determine the energy matrix H_3 it is necessary to evaluate the radial integrals and this involves knowledge of the radial wave functions for each particular atom considered. Slater⁶ has recently given a method for obtaining analytic expressions to represent the Hartree wave functions, and this may be done with great accuracy. A method of interpolation provides wave functions for those atoms for which Hartree has not yet obtained functions. Unfortunately the Hartree functions have not been obtained for the optical electrons and to find wave functions for these electrons demands an extrapolation of Slater's curves which, while it does not give wave functions of as great accuracy as for the inner electrons, still gives greater accuracy than could previously be obtained. Mg I furnishes a good case for comparison with the experimental material. The radial functions given by the Slater method and normalized to unity are: (see Fig. 1)

$$R(3s) = (1/2.84)(-r^3e^{-0.95r} + 11.96r^2e^{-3.92r} - 6.86re^{-11.70r})$$

$$R(3d) = (10^{-3}/1.046)(-r^3e^{-0.70(r-5.71)} - r^3e^{-0.35(r-5.71)})$$

$$R(3p) = (1/2.37)(r^3e^{-1.00r} - 10.43r^2e^{-3.90r}).$$

For these radial integrals it is sufficient to consider only the terms in r^3 , since the other terms have such high negative exponentials and thus contribute only for small r . Since r enters the integrals to a high power this makes the contribution from the terms with high exponentials small.

Experimentally the absolute energy states of Mg I for $3s$ $3d$ and $3p^2$ have been found to be $3s$ $3d$ $^1D = 15,268.9$ $^3D = 13,714.7$ (not separated) and $3p^2$ $^3P_{0,1,2}$ to be 3860.4, 3839.6 and 3799.0 cm^{-1} , respectively. The 1D from $3p^2$ has been reported by Sawyer⁷ but this as pointed out by Paschen⁸ is located too near the triplet. Furthermore, the regularity of the Rydberg denominators convinces one that it is a higher member of the $3s$ nd series. The failure of Paschen to find $3p^2$ 1D may well be due to its great displacement by the perturbation. Knowing the 3D and 3P however

from experiment, it is sufficient, with the knowledge which can be obtained from the radial integral R_b and R_c to determine the parts of the electrostatic energy matrix which are the same for all terms from the same configuration (see Fig. 2a). Calculation of the radial integrals gives $R_b = 10,190$ cm^{-1} , $R_c = 25,620$ cm^{-1} ; $R_e = 29,940$ cm^{-1} , and the difference between the centers of the configurations determined as above is 13,845 cm^{-1} . The electrostatic energy matrix now becomes if we take sd as zero energy for convenience: (Table VII). This energy matrix leads to the following energy values: $^3D_{3,2}$ at -2038 cm^{-1} , 3P_2 at 7857 cm^{-1} and 1D_2 at -6202 cm^{-1} and $+23,282$ cm^{-1} . This places one singlet D at 4000 cm^{-1} below the triplet, a much larger displacement even than is found in experiment. Numerically this is not very good agreement but the difference may easily be due to the extrapolations made in determining the coefficients for the radial wave func-

⁶ J. C. Slater, Phys. Rev. 42, 33 (1932).

⁷ R. A. Sawyer, J. Opt. Soc. Am. 13, 431 (1926).

⁸ F. Paschen, Sitz. Ber. Preuss. Akad. 32, 709 (1931).

TABLE VII. Matrix for H_3 .

	3D_3	3D_2	1D_2	3P_2	1D_2
3D_3	-2038	0	0	0	0
3D_2	0	-2038	0	0	0
1D_2	0	0	2038	0	13230
3P_2	0	0	0	7857	0
1D_2	0	0	13230	0	15043

tions. It is indicated, however, that even for such a case as magnesium for which the p^2 configuration occurs at the ionization potential, the perturbing effect on the sd configuration may be large enough to displace the 1D to a position below 3D .

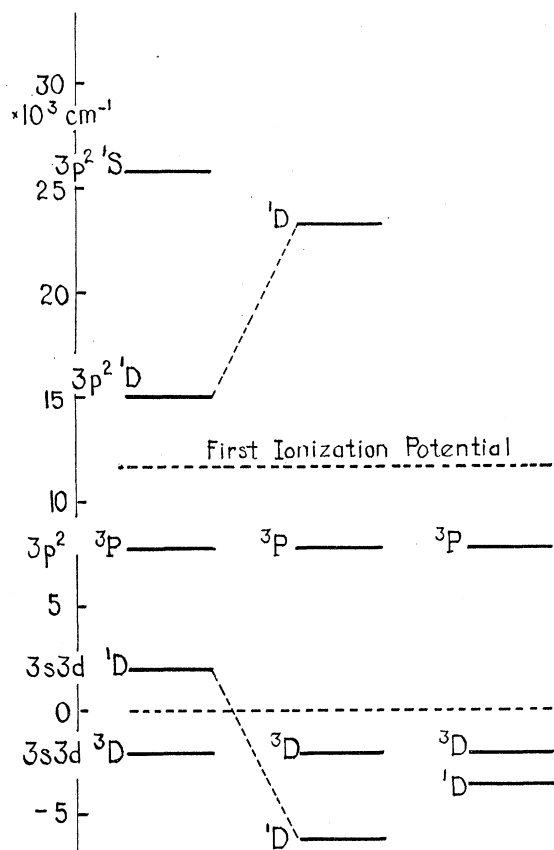


FIG. 2. Energy levels of $3p^2$ and $3s\ 3d$ of Mg I (a) without considering interaction of configurations, (b) with interaction of $3s\ 3d$ and $3p^2$ considered, (c) from experimental material. ${}^3P-{}^3D$ is taken from experiment in *a* and *b*.

PERTURBATION OF THE SERIES $s\ nd$

In order to find how the higher series members are perturbed it is necessary to know the energy matrices of p^2 and $s\ nd$ considered together and also a matrix giving all the $s\ nd$ members to see if the various series members disturb each other. This becomes very complicated when all the series members are considered, and as an approximation only the first two series members will be considered. The matrix of H_3 of $s(n+1)d$ and p^2 is the same as that of $s\ nd$ and p^2 in form and differs only in the fact that $R(n+1)d$ is used in place of $R(nd)$ in determining the various radial integrals. For $s\ nd$ and $s(n+1)d$ considered together H_3 has the following form when transformed to $L-S$ wave functions (see Table VIII). There are components only between like terms in the two configurations. Whether the disturbing effect is much greater between the singlets than between the triplets depends on the size of R_B . A comparison between this matrix and that for $s(n+1)d$ and p^2 taken together would allow one to determine whether perturbation of a series takes place by the perturbing configuration disturbing each configuration of the series separately or only one member of the series is disturbed and this disturbs the others. Since R_B is expected to be positive, any contribution from it would tend to increase the normal singlet-triplet separation of the higher series member. This indicates that the perturbation of a series of terms such as those discussed by Shenstone and Russell⁹ is caused by the separate perturbation of the series members by the perturbing configuration. A calculation of these effects for Mg I indicated that $R(4d)$ was not known with sufficient accuracy to give much significance to the results.

CONCLUSION

It thus seems that it is possible to account for the presence of singlets below their triplets in the two electron spectrum of Mg I by considering the perturbing effect of the low $3p^2$ configuration. It is believed that other examples, Al II, Zn I, Ga II, In II, and others which are similar to Mg I can also be accounted for in this way if the radial

⁹ A. G. Shenstone and H. N. Russell, Phys. Rev. 39, 415 (1932).

TABLE VIII. Matrix of H_3 for $s nd$ and $s(n+1)d$.

	3D_3	$\begin{matrix} s nd \\ {}^3D_2 \end{matrix}$	1D_2	3D_3	$\begin{matrix} s(n+1)d \\ {}^3D_2 \end{matrix}$	1D_2
3D_3	$R_a - \frac{1}{5}R_b$	0	0	$R_A - \frac{1}{5}R_B$	0	0
$s nd {}^3D_2$	0	$R_a - \frac{1}{5}R_b$	0	0	$R_A - \frac{1}{5}R_B$	0
1D_2	0	0	$R_a + \frac{1}{5}R_b$	0	0	$R_A + \frac{1}{5}R_B$
3D_3	$R_A - \frac{1}{5}R_B$	0	0	$R_a' - \frac{1}{5}R_b'$	0	0
$s(n+1)d {}^3D_2$	0	$R_A - \frac{1}{5}R_B$	0	0	$R_a' - \frac{1}{5}R_b'$	0
1D_2	0	0	$R_A + \frac{1}{5}R_B$	0	0	$R_a' + \frac{1}{5}R_b'$

functions are known. There are undoubtedly many other cases where these large interactions of configurations are important and indeed they may account for many of the deviations which have been found from the Slater theory. It seems possible that these interactions may even be large enough to account for the inversion of

doublets in alkali spectra as suggested by White.¹⁰

It is a pleasure to the writer to thank Professor Slater for his interest and criticism as well as for furnishing the radial functions.

¹⁰ H. E. White, Phys. Rev. **40**, 316 (1932).