

Letters to the Editor

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On a New Type of Vector Coupling in Complex Spectra

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TWO types of vector coupling are generally considered by the spectroscopists, the (*LS*) and the (*jj*) coupling; the first takes place when the spin-orbit interaction is weak compared to the electrostatic, the second when the electrostatic interaction is the weaker. We wish to point out that a third type of definite vector coupling is possible, the (*jl*) coupling, which takes place when the electrostatic interaction is weak compared to the spin-orbit interaction of the parent ion, but is strong compared to the spin coupling of the external electron. In this case the total angular momentum *j* of the parent ion and the orbital moment *l* of the external electron are coupled together and have a resultant *K*; then *K* is coupled with the spin of this electron, and their resultant is *J*.

Since the exchange forces act on the spins, it is not sufficient for the extreme (*jl*) coupling that the spin-orbit interaction of the external electron is weak, but also the exchange integrals *G_k* must be small compared to *F₂*; this condition has however a minor importance in the two-electron-like configurations with almost closed shells, since in this case most of the coefficients of *G_k* vanish.

The general structure of a configuration in (*jl*) coupling is a pair structure; these pairs have all the characteristic properties of doublets (line strengths, Zeeman and Paschen-Back effect, etc.) with the only difference that they may have a half-integral *K* and an integral *J* instead of an integral *L* and a half-integral *J*, and that *g(K)* differs generally from unity.

Although this coupling was not yet explicitly used by the spectroscopists, it occurs actually in a number of known spectra: The most striking example is given by the *3d⁹5g* configuration of Cu II, in which Shenstone¹ was unable to resolve the pairs; but also in other configurations of Cu II and of the rare gases the levels tend to occur in pairs. A calculation of the "purity" of the (*jl*) coupling in the *2p⁵(²P_{1/2})nd* configurations of Ne I (as made by Shortley² for the (*jj*) coupling) gives, for instance, a purity of 99–100 percent for the levels with *J*=2 and *J*=3, and of 90–96 percent for those with *J*=1; the

latter deviation is easy to understand, since in this case the effect of *G₁* tends to break the (*jl*) coupling.

Four notations at least were proposed for the levels of this and of similar configurations, but no one was generally accepted, because two are empirical and two, the (*LS*) and the (*jj*) notations, do not give a satisfactory picture of the actual vector coupling; we propose, therefore, that the levels of these configurations should be denoted by the *K* value of their pair: For instance, a suitable form for the notation of the level 12229.82 of Ne I (which was denoted as *3d'₁*, or *3d'₂*, or *3d2a'*) would be (²P_{1/2})3d[2½]₂; the *K* value is written in square brackets, the round brackets being as usual reserved for the term of the parent ion.

The doubling of the levels in the spectra of the rare gases was already pointed out by Shortley and Fried,³ who also calculated the electrostatic interaction in an approximation which corresponds to the above-mentioned conditions for extreme (*jl*) coupling and obtained that in this approximation all levels should be double. Their numerical calculations of the coefficients of Slaters *F²* may be resumed by the formula

$$f_2(jlK) = -\frac{6h^2 + 3h - 2j(j+1)l(l+1)}{4j(j+1)(2l-1)(2l+3)},$$

where

$$h = (j \cdot l) = \frac{K(K+1) - j(j+1) - l(l+1)}{2};$$

this formula is very similar to the corresponding one for the (*LS*) coupling,⁴ and will be demonstrated shortly in another paper.

The *g* values in (*jl*) coupling may be calculated with the ordinary methods of vector coupling; the result is

$$g = \frac{2J+1}{2K+1} + 2 \frac{K(K+1) + j(j+1) - l(l+1)}{(2K+1)(2J+1)} (g_j - 1),$$

where *g_j* is the *g* factor of the parent ion.

The agreement with the experimental values is, of course, not so good as that of the *g* values calculated with the actual eigenfunctions;⁵ nevertheless, owing to its simplicity and to its independence from the coupling parameters, this formula may be helpful to the spectroscopists for the classification of new spectra.

¹ Shenstone, Trans. Roy. Soc. A235, 195 (1936).

² G. H. Shortley, Phys. Rev. 44, 666 (1933).

³ G. H. Shortley and B. Fried, Phys. Rev. 54, 749 (1938).

⁴ G. Racah, Phys. Rev. 61, 537 (1942).

⁵ J. B. Green and J. A. Peoples, Jr., Phys. Rev. 54, 602 (1938); J. B. Green and B. Fried, Phys. Rev. 54, 876 (1938).

On the Deep Configuration of Cobalt

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A RECENT paper of Russell, King, and Moore¹ (RKM) gives a very extensive classification of the spectrum of Co I; some assignments of terms to high configurations are given as tentative, but the assignments to the deep configurations are given as definitive, because the theoretical paper of Marvin² is considered as conclusive. We wish to point out that Marvin's results do not seem