Without any loss of generality we may therefore represent the deviations from Slater's formulas in d^2 by

$$2\alpha(\mathbf{l}_1\cdot\mathbf{l}_2)+\beta q_{12},$$

where q is the operator, already defined elsewhere,[3] which vanishes for $L\neq 0$ and equals 5 for the S-state. Then, according to our assumption, the deviations in the configuration d^n will be represented by

$$\sum_{i<k}[2\alpha(\mathbf{l}_i\cdot\mathbf{l}_k)+\beta q_{ik}]=\alpha[L(L+1)-6n]+\beta Q.$$

As Q is different from zero only for the higher terms of every configuration and vanishes or has very small expectation values for almost all the terms which are experimentally known, the second correction has no practical importance, and the only important one is the $L(L+1)$ correction.

It may also be pointed out that this correction explains the constancy of the ratio $(^1S-{}^1D)/(^1D-{}^3P)$ in the configurations $2p^2$ and $2p^4$ of the first period, and predicts that the ratio $(^2P-{}^2D)/(^2D-{}^4S)$ in the configuration $2p^3$ should be 4/9 of the former ratio, in excellent agreement with the experimental data.[4]

[1] R. E. Trees, Phys. Rev. **83**, 756 (1951).
[2] E. U. Condon and G. H. Shortley, *Theory of Atomic Spectra* (Cambridge University Press, London, 1935), p. 203.
[3] G. Racah, Phys. Rev. **62**, 438 (1942), Eq. (90), and **63**, 367 (1943), Eq. (35).
[4] See reference 2, p. 198.

The $L(L+1)$ Correction to the Slater Formulas for the Energy Levels

R. E. TREES*
University of Pennsylvania, Philadelphia, Pennsylvania
(Received November 23, 1951)

IN recent papers[1,2] it has been pointed out that a correction of form $\alpha L(L+1)$ produces greatly improved agreement between theoretical and experimental term values in the configuration d^5s of Mn II and Fe III. This correction represents a polarization energy, and rigorous treatment of second-order effects is difficult even for the highly simplified wave functions of electrons in a solid.[3] No satisfactory simple theory to explain this effect has as yet been found, but the following comments may be helpful.

The fact that the errors in all configurations of type $3d^n$ decrease as L increases has already been noted.[2] A variation independent of spin and proportional to $L(L+1)$ was, however, felt to be quantitatively justifiable only for the d^5 configuration. In the d^6 configuration of Fe III a correction proportional to $L(L+1)$ reduces the mean deviation only from ± 876 cm^{-1} [4] to ± 439 cm^{-1}.[5] This is a relatively small improvement compared to the reduction from ± 852 cm^{-1} to ± 105 cm^{-1} found in the d^5s configuration of Fe III. The value of α in the d^6 configuration, namely 67.4, is consistent with the value 80.7 in the d^5s configuration. This, together with the similarity of the trend in the errors for all $3d^n$ configurations, indicates that the corrections are at least approximately related according to the theory just advanced by Racah[6] in which the polarization energy is treated linearly. However, as his theory leads essentially to a correction of form $L(L+1)$ for all configurations, it will not realize the full possibilities for accurate prediction of levels to ± 100–200 cm^{-1} in the $3d^6$ configuration of Fe III.

A basis for the favored position of the d^5 configuration relative to the d^6 configuration exists in the fact that in the former case most of the term values are rational functions of the Slater integrals (i.e., the eigenfunctions are characterized by a single seniority number,[7] whereas most of the d^6 eigenfunctions are linear combinations of states with two seniority numbers). The one term with an irrational theoretical value in the $3d^54s$ configuration of Fe III for which an unperturbed experimental value is available is the $3d^5(a^2D)4s$, c^3D. For this term the error was $+442$ cm^{-1} while for all other levels the absolute value of the errors was less than 200 cm^{-1}. It seems likely from this that the correction of form $\alpha L(L+1)$ applies only to terms that are rational functions of the Slater parameters.

This conclusion can be checked very nicely in the $3d^6$ configuration of Fe III against the 6 rational levels for which experimental values are available. A correction proportional to $L(L+1)$ need not be applied to the usual Slater formulas, as such a correction can be absorbed in the values of the parameters A, B, C.[8] These 6 levels can be fitted with a mean deviation of ± 150 cm^{-1}, and no deviation exceeds 200 cm^{-1} in absolute value.[9] This is to be compared with the deviation of ± 876 cm^{-1} in fitting all levels.

The correction to be applied when the term value is not a rational function of the Slater parameters, so that agreement of equal accuracy will be obtained, has not yet been found. However, if the eigenfunction is

$$C_1\psi(d^nv_1SL)+C_2\psi(d^nv_2SL),$$

a correction of form

$$(1+2C_1C_2)\alpha L(L+1)$$

will produce close agreement in the $3d^5(a^2D)4s$, c^3D term discussed previously. A check of the validity of this correction in the d^6 configuration has not yet been made. In any event, it does not seem likely that the extra refinement needed to get a correction for levels with irrational term values can be derived theoretically by treating the polarization energy linearly.

* Now at the National Bureau of Standards, Washington, D. C.
[1] R. E. Trees, Phys. Rev. **83**, 756 (1951).
[2] R. E. Trees, Phys. Rev. **84**, 1089 (1951).
[3] E. Wigner, Phys. Rev. **46**, 1002 (1934); W. Macke, Z. Naturforsch. **5a**, No. 4, 192 (1950).
[4] R. E. Trees, Phys. Rev. **82**, 683 (1951).
[5] Values of the parameters are $A=19{,}969$, $B=953$, $C=3652$, $\alpha=67$.
[6] G. Racah, Phys. Rev. **85**, 381 (1951).
[7] The seniority number is introduced by G. Racah, Phys. Rev. **63**, 367 (1943).
[8] For instance, a $d^6\,{}^3H$ term has the energy $(A-17B+4C)$; with an $\alpha L(L+1)$ correction this becomes

$$A-17B+4C+30\alpha=(A-36\alpha)-17(B-2\alpha)+4(C+8\alpha).$$

The four parameters A, B, C, α are thus replaced by the three parameters $A-36\alpha$, $B-2\alpha$, $C+8\alpha$. This same substitution applies in all six levels.
[9] Values of the parameters are $A=18{,}400$, $B=853$, $C=4116$.

The Magnetic Threshold Field Curve of a Superconductor

R. P. HUDSON
Cryogenics Section, National Bureau of Standards, Washington, D. C.
(Received November 15, 1951)

A NUMBER of authors[1] have considered the relation between the shape of the critical field *vs* temperature curve of a superconductor and the temperature dependence of the specific heat in both normal and superconducting states, from somewhat different points of view. In general, however, use is made of the Gorter-Casimir thermodynamic formulas[2] together with the assumption of a parabolic shape for the H_c *vs* T curve to obtain the familiar expression

$$\gamma=VH_0^2/2\pi T_0^2, \tag{1}$$

where γ is the "Sommerfeld term" (for the normal state), H_0 is the value of H_c at the absolute zero, V is the atomic volume, and T_0 is the zero-field transition temperature.

The complete expression one obtains is

$$\Delta C=C_s-C_n=-(VH_0^2/2\pi T_0^2)T+(3VH_0^2/2\pi T_0^4)T^3 \tag{2}$$

and on the assumption that C_n contains only a lattice term plus the Sommerfeld term, while C_s contains the same lattice term plus a T^3-term for the electron assembly, one derives relation (1) above; i.e., the linear term in (2) is identified with $-\gamma T$. We then have

$$\Delta C=-\gamma T+(3\gamma/T_0^2)T^3. \tag{3}$$