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ENERGY RELATIONS IN COMPLEX SPECTRA

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Abstract

The manner in which the energy levels of extreme (jj) coupling are split up by interaction of the electrons is calculated, and the results serve in special cases to determine energies in the condition intermediate between (jj) and (LS) coupling. Single-electron wave functions appropriate to large spin-orbit interaction are selected, and antisymmetric atomic wave functions are formed of them. With these the diagonal elements of the matrix of electrostatic interaction are reduced to combinations of radial integrals, the same integrals met by Slater in (LS) coupling. Some configurations have only one such radial integral to express electrostatic interaction. It serves as a parameter in the extension to intermediate coupling by a method of Goudsmit. Coefficients in the general equation for the energies are determined by the energies in extreme couplings. Knowledge of electrostatic energies in (jj) coupling, as here calculated, extends the applicability of the method to configurations having three states with the same angular momentum.

Introduction

THEORETICAL relationships between the separations of the levels of a configuration in the two extreme couplings are well known.[1,2] They are obtained by considering a single type of interaction at a time. Houston introduced both electrostatic and spin-orbit interaction and solved completely the problem of two electrons, one of them an s-electron. The energies of the two states with the same J are solutions of a ternary quadratic equation. Goudsmit[3] has suggested a simplified method of solution for such problems. Even in more complicated configurations the energies are roots of homogeneous equations, and in some cases it is possible to determine the coefficients from a knowledge of the energies in extreme couplings. For several configurations, the separations due to spin-orbit interaction are known in terms of a parameter both in (jj) coupling, where they are large, and in (LS) coupling, where they are relatively small. The electrostatic separations are known in extreme (LS) coupling, where they are large.[1] This knowledge sufficed to determine the coefficients for the configurations p^2 and p^4, where the equations for general coupling are quadratic or linear. It will be shown that knowledge of the electrostatic energies in (jj) coupling, where they are small, completes the determination of the coefficients of a cubic equation with one electrostatic parameter. The ensuing calculation of such energies will thus make it possible to determine for intermediate coupling the levels of some configurations having three states with the same value of J.

[1] J. C. Slater, Phys. Rev. **34**, 1293 (1929).

[2] Pauling and Goudsmit, Theory of Line Spectra, McGraw-Hill, 1930.

[3] S. Goudsmit, Phys. Rev. **35**, 1325 (1930).

ELECTROSTATIC ENERGY IN (*jj*) COUPLING

1. Wave functions for (jj) coupling. The calculation of the electrostatic energy of the states is quite similar to that done by Slater for (*LS*) coupling, but here the appropriate wave functions are less simple. We are dealing with the smaller of two interactions. First we determine the wave functions stabilized for the larger spin-orbit interaction. This initial perturbation is a sum of functions of single-electron coordinates. The problem thus reduces to the selection of single-electron wave functions $u(nljm_j/)$ appropriate to spin-orbit interaction. Each such stabilized wave function is a linear combination of the two[4] simple single-electron wave functions $u(nlm_l m_s/)$ with the same value of total angular momentum m_j. These are $u(nlm_j-\frac{1}{2}/r\theta\phi)\ \delta(\frac{1}{2}/\sigma)$ and $u(nlm_j+\frac{1}{2}/r\theta\phi)\ \delta(-\frac{1}{2}/\sigma)$ which we abbreviate $u(m_j-\frac{1}{2}/)\ \delta(\frac{1}{2}/\sigma)$ and $u(m_j+\frac{1}{2}/)\ \delta(-\frac{1}{2}/\sigma)$. To calculate the perturbation energy matrix $v_{ij} = \int u(i/)\ (\mathbf{l}\cdot\mathbf{s})\ u(j/)$ we use the relations

$$l_x \pm i l_y = e^{\pm i\phi}\left(\pm\frac{\partial}{\partial\theta} + i\frac{\cos\theta}{\sin\theta}\frac{\partial}{\partial\phi}\right); \quad l_z = -i\frac{\partial}{\partial\phi}$$

$$\frac{\partial}{\partial\theta}P_l^m(\cos\theta) = m\frac{\cos\theta}{\sin\theta}P_l^m(\cos\theta) - P_l^{m+1}(\cos\theta).$$

With these and the operators[5] representing spin we obtain

$$v_{11} = \tfrac{1}{2}(m_j - \tfrac{1}{2});\quad v_{22} = -\tfrac{1}{2}(m_j + \tfrac{1}{2})$$
$$v_{21} = v_{12} = \mp\tfrac{1}{2}\{(l - m_j + \tfrac{1}{2})(l + m_j + \tfrac{1}{2})\}^{1/2}.$$

Of the double sign here and in the following formulas, the upper sign is for positive values of m_j, the lower for negative m_j. (Positive roots of the radicals are implied). In either case the energies are $\frac{1}{2}l,\ -\frac{1}{2}(l+1)$. The normalized linear combinations are

$$(2l+1)^{-1/2}\{(l + m_j + \tfrac{1}{2})^{1/2}u(m_j - \tfrac{1}{2}/)\delta(\tfrac{1}{2}/\sigma) \mp (l - m_j + \tfrac{1}{2})^{1/2}u(m_j + \tfrac{1}{2}/)\delta(-\tfrac{1}{2}/\sigma)\}$$
$$(2l+1)^{-1/2}\{(l - m_j + \tfrac{1}{2})^{1/2}u(m_j - \tfrac{1}{2}/)\delta(\tfrac{1}{2}/\sigma) \pm (l + m_j + \tfrac{1}{2})^{1/2}u(m_j + \tfrac{1}{2}/)\delta(-\tfrac{1}{2}/\sigma)\}.$$

In each case the first combination belongs to the state with $j = l+\frac{1}{2}$, the second has $j = l-\frac{1}{2}$. The stabilized wave function may then be written as an explicit expression in its quantum numbers, as follows:

$$u(nljm_j/) = (2l+1)^{-1/2}\{[l + \tfrac{1}{2} + 2(j-l)m_j]^{1/2}u(nlm_j - \tfrac{1}{2}/)\delta(\tfrac{1}{2}/\sigma) - 2(j-l)(m_j/|m_j|)[l + \tfrac{1}{2} - 2(j-l)m_j]^{1/2}u(nlm_j + \tfrac{1}{2}/)\delta(-\tfrac{1}{2}/\sigma)\} \quad (1)$$

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[4] J. H. Bartlett, Jr., Phys. Rev. **35**, 230 (1930).

[5] A convenient explicit formulation of the Pauli spin operations is:

$$s_x\delta(m_s/\sigma) = \tfrac{1}{2}\delta(m_s/-\sigma)$$
$$s_y\delta(m_s/\sigma) = im_s\delta(m_s/-\sigma)$$
$$s_z\delta(m_s/\sigma) = m_s\delta(m_s/\sigma)$$

where the unit is $h/2\pi$ and $m_s = \pm\frac{1}{2}$.

The coefficients may be abbreviated:

$$u(n'l'j'm_j'/) = f'u(m_j' - \tfrac{1}{2}/)\delta(\tfrac{1}{2}/\sigma) + g'u(m_j' + \tfrac{1}{2}/)\delta(-\tfrac{1}{2}/\sigma). \qquad (1')$$

The two functions $u(m_j - \frac{1}{2}/\ )$ and $u(m_j + \frac{1}{2}/\ )$ have the same radial part, so the radial part of the stabilized function may be separated from the rest. This fact later assumes importance in leading us to the radial integrals of Slater's paper.

2. Electrostatic energy. The next step is identical with a part of Slaters' work (reference 1, Part 2, §2), being independent of the specialization of the single-electron wave functions. $u(n/\ )$ may be the wave function for any state of which the four quantum numbers are represented by n. The fundamental states of the atom have as wave functions antisymmetric cominations of products of these single-electron wave functions. The integrals $\int u^*Hu$ contain many terms, the number of which is reduced by consideration of the orthogonality of the electronic wave functions. The diagonal elements of the matrix of electrostatic interaction reduce to

$$\sum(\text{pairs of } n\text{'s})\{J(n;\, n') - K(n;\, n')\}$$

where

$$\begin{aligned} J(n;\, n') &= \int u^*(n/1)u^*(n'/2)(e^2/r_{12})u(n/1)u(n'/2) \\ K(n;\, n') &= \int u^*(n/1)u^*(n'/2)(e^2/r_{12})u(n/2)u(n'/1). \end{aligned} \qquad (2)$$

3. Energy in (jj) coupling. The integrals (2) must now be determined for the special case of (jj) coupling. The electron wave functions $u(n/\ )$ are $u(nljm_j/\ )$ of (1). A summation over the spin coordinates accompanies the integration. The summation having been made; $K(nljm_j;\, n'l'j'm_j') =$

$$\begin{aligned} &f^2f'^2 \int (e^2/r_{12})u^*(m_j - \tfrac{1}{2}/1)u^*(m_j' - \tfrac{1}{2}/2)u(m_j - \tfrac{1}{2}/2)u(m_j' - \tfrac{1}{2}/1) \\ &+ fg'gf \int (e^2/r_{12})u^*(m_j - \tfrac{1}{2}/1)u^*(m_j' + \tfrac{1}{2}/2)u(m_j + \tfrac{1}{2}/2)u(m_j' - \tfrac{1}{2}/1) \\ &+ gf'fg' \int (e^2/r_{12})u^*(m_j + \tfrac{1}{2}/1)u(m_j' - \tfrac{1}{2}/2)u(m_j - \tfrac{1}{2}/2)u(m_j' + \tfrac{1}{2}/1) \\ &+ g^2g'^2 \int (e^2/r_{12})u^*(m_j + \tfrac{1}{2}/1)u(m_j' + \tfrac{1}{2}/2)u(m_j + \tfrac{1}{2}/2)u(m_j' + \tfrac{1}{2}/1) \\ &\quad = f^2f'^2K(nlm_j - \tfrac{1}{2};\, n'l'm_j' - \tfrac{1}{2}) + g^2g'^2K(nlm_j + \tfrac{1}{2};\, n'l'm_j' + \tfrac{1}{2}) \\ &\qquad + ff'gg'L(nlm_j;\, n'l'm_j') \end{aligned} \qquad (3)$$

where

$$L(nlm_j;n'l'm_j') = 2\int (e^2/r_{12})u^*(m_j - \tfrac{1}{2}/1)u^*(m_j' + \tfrac{1}{2}/2)u(m_j + \tfrac{1}{2}/2)u(m_j' - \tfrac{1}{2}/1)$$

Similarly,

$$\begin{aligned} J(nljm_j;\, n'l'j'm_j') &= f^2f'^2J(nlm_j - \tfrac{1}{2};\, n'l'm_j' - \tfrac{1}{2}) \\ &+ f^2g'^2J(nlm_j - \tfrac{1}{2};\, n'l'm_j' + \tfrac{1}{2}) + g^2f'^2J(nlm_j + \tfrac{1}{2};\, n'l'm_j' - \tfrac{1}{2}) \\ &+ g^2g'^2J(nlm_j + \tfrac{1}{2};\, n'l'm_j' + \tfrac{1}{2}). \end{aligned} \tag{4}$$

The integrals J and K are Slater's integrals. He has tabulated the results of the angular integrations. L is a new integral. It contains, in general, four different sets of unperturbed, single-electron quantum numbers nlm_l. There are, however, only two different sets of principal quantum numbers nl, so that the radial integrals are the same as some of those that Slater met. Introducing the expansion for $(1/r_{12})$ into the definition of L, along with the spherical harmonics for $u(nlm_l/—)$, we get

$$\begin{aligned} L(m_j;\, m_j') &= L(nlm_j;\, n'l'm_j') \\ &= c^k(lm_j - \tfrac{1}{2};\, l'm_j' - \tfrac{1}{2})c^k(lm_j + \tfrac{1}{2};\, l'm_j' + \tfrac{1}{2})G^k(nl,\, n'l') \end{aligned}$$

where

$$\begin{aligned} c^k(lm;\, l'm') = \frac{1}{2}\left\{\frac{(k - |\, m - m' \,|)!}{(k + |\, m - m' \,|)!}\right\}^{1/2} \left\{(2l + 1)\frac{(l - |\, m \,|)!}{(l + |\, m \,|)!}\right\}^{1/2} \\ \left\{(2l' + 1)\frac{(l' - |\, m' \,|)!}{(l' + |\, m' \,|)!}\right\}^{1/2} \int_{-1}^{1} P_l^{|m|}(x)P_{l'}^{|m'|}(x)P_k^{|m-m'|}(x)dx \end{aligned}$$

$G^k(nl,\, n'l')$ is a radial "exchange" integral defined by Slater. (If we consider the radial wave function $R(nl/r)$ normalized to unity,[6] we define F^k and G^k without the factor $(4\pi)^2$). It is entirely fitting that we should have the same radial integrals in the two extreme couplings; another result would be inconsistent with sum rules.

The coefficients c^k are related thus to Slater's coefficients:

$$\begin{aligned} a^k(lm,\, l'm') &= c^k(lm,\, lm)c^k(l'm',\, l'm') \\ b^k(lm,\, l'm') &= \{c^k(lm,\, l'm')\}^2 \end{aligned}$$

c^k may thus be had, except for sign,[7] by taking the square roots of the values of b^k tabulated by Slater.

(2) says that the energy is the sum of the interactions of pairs of electrons. The interaction energy of two electrons in specified states is had by evaluating (3) and (4) with the aid of tables of a^k, b^k, and c^k. The energies so calculated for electrons in the various s, p, and d states, are listed in Table I.

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[6] Condon and Shortley, Phys. Rev. **37,** 1025 (1931); §2.

[7] To get c^k, the square root of b^k is to be taken with the negative sign for the following values of $(l,\, m;\, l',\, m';\, k)$: $(1,\, \pm 1;\, 1,\, \pm 1;\, 2)$, $(1,\, \pm 1;\, 2,\, \pm 1$ or $\pm 2;\, 3)$, $(1,\, \pm 1;\, 2,\, 0;\, 1)$, $(2,\, \pm 2;\, 2,\, \pm 2;\, 2)$, $(2,\, \pm 2;\, 2,\, \pm 1;\, 4)$, $(2,\, \pm 2;\, 2,\, 0;\, 2)$, $(2,\, \pm 2;\, 2,\, \pm 1;\, 4)$, and $(2,\, \pm 1;\, 2,\, \pm 1;\, 4)$; otherwise positive. Also, $b^3(1,\, \pm 1;\, 2,\, \pm 2)$ is 45/245, not 9/245. The formulation of c^k was suggested by consideration of non-diagonal matrix elements by workers at M.I.T. and Harvard, kindly communicated by M. H. Johnson.

TABLE I. *Interaction energy of pairs of electrons.*
(NOTE: the table is also valid when the signs both of m_j and of m_j' are changed.)

	l	j	m_j	l'	j'	m_j'	$-G^0$	$-G^1/9$	$-G^2/25$
ss	0	1/2	1/2	0	1/2	1/2	1	0	0
	0	1/2	1/2	0	1/2	-1/2	0	0	0
ps	1	3/2	3/2	0	1/2	1/2	0	3	0
	1	3/2	3/2	0	1/2	-1/2	0	0	0
	1	3/2	1/2	0	1/2	1/2	0	2	0
	1	3/2	1/2	0	1/2	-1/2	0	1	0
	1	1/2	1/2	0	1/2	1/2	0	1	0
	1	1/2	1/2	0	1/2	-1/2	0	2	0
ds	2	5/2	5/2	0	1/2	1/2	0	0	5
	2	5/2	5/2	0	1/2	-1/2	0	0	0
	2	5/2	3/2	0	1/2	1/2	0	0	4
	2	5/2	3/2	0	1/2	-1/2	0	0	1
	2	5/2	1/2	0	1/2	1/2	0	0	3
	2	5/2	1/2	0	1/2	-1/2	0	0	2
	2	3/2	3/2	0	1/2	1/2	0	0	1
	2	3/2	3/2	0	1/2	-1/2	0	0	4
	2	3/2	1/2	0	1/2	1/2	0	0	2
	2	3/2	1/2	0	1/2	-1/2	0	0	3
	l	j	m_j	l'	j'	m_j'	$F^2/25$	$-G^0$	$-G^2/25$
pp	1	3/2	3/2	1	3/2	3/2	1	1	1
	1	3/2	3/2	1	3/2	1/2	-1	0	2
	1	3/2	3/2	1	3/2	-1/2	-1	0	2
	1	3/2	3/2	1	3/2	-3/2	1	0	0
	1	3/2	3/2	1	1/2	1/2	0	0	1
	1	3/2	3/2	1	1/2	-1/2	0	0	4
	1	3/2	1/2	1	3/2	1/2	1	1	1
	1	3/2	1/2	1	3/2	-1/2	1	0	0
	1	3/2	1/2	1	1/2	1/2	0	0	2
	1	3/2	1/2	1	1/2	-1/2	0	0	3
	1	1/2	1/2	1	1/2	1/2	0	1	0
	1	1/2	1/2	1	1/2	-1/2	0	0	0
	l	j	m_j	l'	j'	m_j'	$F^2/105$	$-G^1/225$	$-G^3/1225$
dp	2	5/2	5/2	1	3/2	3/2	10	90	15
	2	5/2	5/2	1	3/2	1/2	-10	0	50
	2	5/2	5/2	1	3/2	-1/2	-10	0	75
	2	5/2	5/2	1	3/2	-3/2	10	0	0
	2	5/2	5/2	1	1/2	1/2	0	0	25
	2	5/2	5/2	1	1/2	-1/2	0	0	150
	2	5/2	3/2	1	3/2	3/2	-2	36	36
	2	5/2	3/2	1	3/2	1/2	2	54	49
	2	5/2	3/2	1	3/2	-1/2	2	0	10
	2	5/2	3/2	1	3/2	-3/2	-2	0	45
	2	5/2	3/2	1	1/2	1/2	0	0	50
	2	5/2	3/2	1	1/2	-1/2	0	0	125
	2	5/2	1/2	1	3/2	3/2	-8	9	54
	2	5/2	1/2	1	3/2	1/2	8	54	24
	2	5/2	1/2	1	3/2	-1/2	8	27	2
	2	5/2	1/2	1	3/2	-3/2	-8	0	60
	2	5/2	1/2	1	1/2	1/2	0	0	75
	2	5/2	1/2	1	1/2	-1/2	0	0	100
	2	3/2	3/2	1	3/2	3/2	7	9	9
	2	3/2	3/2	1	3/2	1/2	-7	6	36
	2	3/2	3/2	1	3/2	-1/2	-7	0	90
	2	3/2	3/2	1	3/2	-3/2	7	0	180
	2	3/2	3/2	1	1/2	1/2	0	75	0
	2	3/2	3/2	1	1/2	-1/2	0	0	0
	2	3/2	1/2	1	3/2	3/2	-7	6	36
	2	3/2	1/2	1	3/2	1/2	7	1	81
	2	3/2	1/2	1	3/2	-1/2	7	8	108
	2	3/2	1/2	1	3/2	-3/2	-7	0	90
	2	3/2	1/2	1	1/2	1/2	0	50	0
	2	3/2	1/2	1	1/2	-1/2	0	25	0

TABLE I. (*continued*)

	l	j	m_j	l'	j'	m_j'	$F^2/1225$	$F^4/441$	$-G^0$	$-G^2/1225$	$-G^4/441$
dd	2	5/2	5/2	2	5/2	5/2	100	1	1	100	1
	2	5/2	5/2	2	5/2	3/2	−20	−3	0	120	4
	2	5/2	5/2	2	5/2	1/2	−80	2	0	60	9
	2	5/2	5/2	2	5/2	−1/2	−80	2	0	0	14
	2	5/2	5/2	2	5/2	−3/2	−20	3	0	0	14
	2	5/2	5/2	2	5/2	−5/2	100	1	0	0	0
	2	5/2	3/2	2	5/2	3/2	4	9	1	4	9
	2	5/2	3/2	2	5/2	1/2	16	−6	0	48	10
	2	5/2	3/2	2	5/2	−1/2	16	−6	0	108	5
	2	5/2	3/2	2	5/2	−3/2	4	9	0	0	0
	2	5/2	1/2	2	5/2	1/2	64	4	1	64	4
	2	5/2	1/2	2	5/2	−1/2	64	4	0	0	0
	2	5/2	5/2	2	3/2	3/2	70	0	0	30	1
	2	5/2	5/2	2	3/2	1/2	−70	0	0	40	6
	2	5/2	5/2	2	3/2	−1/2	−70	0	0	0	21
	2	5/2	5/2	2	3/2	−3/2	70	0	0	0	56
	2	5/2	3/2	2	3/2	3/2	−14	0	0	36	4
	2	5/2	3/2	2	3/2	1/2	14	0	0	2	15
	2	5/2	3/2	2	3/2	−1/2	14	0	0	32	30
	2	5/2	3/2	2	3/2	−3/2	−14	0	0	0	35
	2	5/2	1/2	2	3/2	3/2	−56	0	0	27	10
	2	5/2	1/2	2	3/2	1/2	56	0	0	6	24
	2	5/2	1/2	2	3/2	−1/2	56	0	0	25	30
	2	5/2	1/2	2	3/2	−3/2	−56	0	0	12	20
	2	3/2	3/2	2	3/2	3/2	49	0	1	49	0
	2	3/2	3/2	2	3/2	1/2	−49	0	0	98	0
	2	3/2	3/2	2	3/2	−1/2	−49	0	0	98	0
	2	3/2	3/2	2	3/2	−3/2	49	0	0	0	0
	2	3/2	1/2	2	3/2	1/2	49	0	1	49	0
	2	3/2	1/2	2	3/2	−1/2	49	0	0	0	0

The first columns list the quantum numbers specifying a pair of electronic states, and they are followed in the other columns by the energy coefficients belonging to the pair of states. To get the interaction energy of the states, $J(nljm_j;\, n'l'j'm_j') - K(nljm_j;\, m'l'j'm_j')$, we multiply the integral at the head of each column by the coefficient listed in its column, and add the products. In the case of more than two electrons, we must make a summation of these energies over the pairs of electron states, according to (2).

This gives us the diagonal elements of the matrix of interaction energy. Because the wave functions are stabilized for spin-orbit interaction, non-diagonal elements exist only between states of the same magnetic energy—the states that are degenerate at the introduction of our present perturbation. M_J is a constant of the motion, so the energy matrix is considered only in the squares characterized by the same set of $(nlj)(n'l'j') \cdots (n''l''j'')$ and the same M_J. The sum of the diagonal terms, which we now know, is the sum of the energies of the states with this set of electronic quantum numbers and with $J \geqq M_J$. By taking differences[8] of such diagonal sums we get energies of the individual states $(nlj)(n'l'j') \cdots (n''l''j'')J$.

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[8] Example: In Table II, the $J=4$ level of *pd* has the energy of the first *dp* state of Table I. The sum of the energies of this and the next level, $J=3$, is the sum of the second and seventh *dp* states of Table I, namely, $-12\, F^2/105 - 36\, G^1/225 - 86\, G^3/1225$; and this, minus the energy for $J=4$, is the energy for the $J=3$ level.

4. Examples of electrostatic separations in (jj) coupling. This calculation has been carried out for several configurations, involving the interactions of two, three, or six electrons. When the optical electrons are an almost-closed shell and one other electron, as in the configuration p^5p', there are two sets of parameters of electrostatic interaction. The integrals $F^k(nl, nl)$ and $G^k(nl, nl)$ express the interaction of the equivalent electrons in the almost-closed shell, and in the result contribute the same energy to each level of the configuration, so do not affect the separations. The integrals $F^k(nl, n'l')$ and $G^k(nl, n'l')$ express the interaction of the single electron with the electrons of the almost-closed shell, and give interesting separations.

Fig. 1 illustrates schematically the roles played by the electrostatic and spin-orbit interactions near extreme couplings, for the example p^5d. The calculations described above give the coefficients of $F^k(nl; n'l')$ and $G^k(nl; n'l')$ listed on the left side, and for the right side the method of Slater is used. a_p and a_d are the usual parameters of spin-orbit interaction ($energy = a_p (l_p \cdot s_p)$) and their contributions are given by the vector model. ($J=4$) has been taken as reference level.

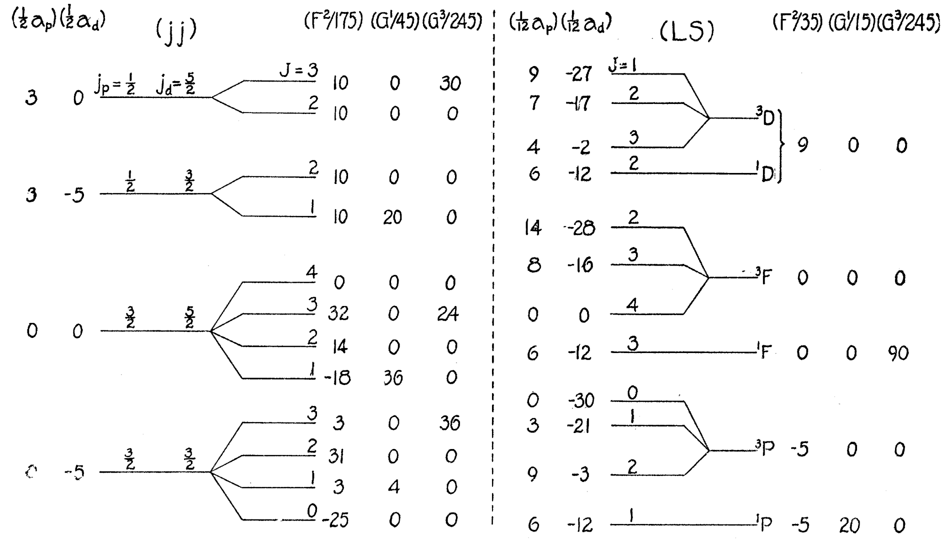

Fig. 1. Energy scheme of p^5d near extreme couplings.

The (jj) electrostatic energies for the configurations pp', pd, dd', p^5s, and p^5p' are given in Table II. Corresponding energies in (LS) coupling, with which comparison may be made as regards sum rules, have been given by Slater[1] or by Condon and Shortley,[6] except for p^5p and p^5d. For p^5d they are listed in Fig. 1, and for p^5p they are

$$^1S,\ ^3S = -2F^2/5 + 2G^0 - 2G^2/5 \pm 3G^0$$

$$^1P,\ ^3P = F^2/5 - G^0 - 2G^2/5$$

$$^1D,\ ^3D = -F^2/25 - G^0 - 4G^2/25 \pm 6G^2/25.$$

In the case of p^5d it happens that the four levels with $J=2$ involve only one parameter of electrostatic interaction. For p^5s and d^9s the results are just the same as for ps and ds, respectively, and the latter have been given by Houston. Experiment shows that the integral $G^k(nl;\, n'O)$ changes its sign between these cases,[9] due to the change in the radial parts of the electronic wave functions.

TABLE II. *Electrostatic energies for various configurations*

			pp'		
j	j'	J	$F^2/25$	G^0	$G^2/25$
3/2	3/2	3	1	−1	−1
		2	−3	1	−3
		1	1	−1	−1
		0	5	1	5
3/2	1/2	2	0	0	−1
		1	0	0	−5
1/2	3/2	2	0	0	−1
		1	0	0	−5
1/2	1/2	1	0	−1	0
		0	0	1	0

			p^5p		
j	j'	J	$F^2/25$	G^0	$G^2/25$
3/2	3/2	3	−1	−1	−10
		2	3	−1	− 6
		1	−1	−1	−10
		0	−5	3	−10
3/2	1/2	2	0	−1	− 6
		1	0	−1	−10
1/2	3/2	2	0	−1	− 6
		1	0	−1	−10
1/2	1/2	1	0	−1	−10
		0	0	1	−10

			pd		
j_p	j_d	J	$F^2/175$	$-G^1/225$	$-G^3/1225$
3/2	5/2	4	10	90	15
		3	−22	−54	71
		2	− 4	27	92
		1	28	− 9	−84
3/2	3/2	3	7	9	9
		2	−21	3	63
		1	7	−11	189
		0	35	15	315
1/2	5/2	3	0	0	25
		2	0	0	175
1/2	3/2	2	0	25	0
		1	0	−25	0

				dd'			
j	j'	J	$F^2/25$	$F^4/49$	G^0	$G^2/1225$	$G^4/441$
5/2	5/2	5	100	1	−1	−100	− 1
		4	−140	− 7	1	−140	− 7
		3	−116	19	−1	116	−19
		2	28	−21	1	28	−21
		1	184	− 6	−1	−184	6
		0	280	42	1	280	42
5/2	3/2	4	70	0	0	− 30	− 1
		3	−154	0	0	− 46	− 9
		2	− 28	0	0	47	−36
		1	196	0	0	− 21	−84
3/2	5/2	4	70	0	0	− 30	− 1
		3	−154	0	0	− 46	− 9
		2	− 28	0	0	47	−36
		1	196	0	0	− 21	−84
3/2	3/2	3	49	0	−1	− 49	0
		2	−147	0	1	−147	0
		1	49	0	−1	− 49	0
		0	245	0	1	245	0

When neither of the electrons is in an s state, (jj) coupling is not realized in the extant spectral data. In configurations like p^5d, the greater effective nuclear charge for the equivalent electrons augments one of the parameters of magnetic coupling, but the other remains small so that the four groups overlap in pairs. Comparison with experiment is therefore possible only after an extension of the results to intermediate coupling, similar to that which follows.

ENERGY IN INTERMEDIATE COUPLING

5. Combined perturbations.[10] In intermediate coupling, the perturbation potential is a sum of two terms depending differently on the coordinates, $H'=v+w$. v and w are the spin-orbit and the electrostatic interaction. Among atoms with the same optical-electron configuration, the unperturbed wave functions differ from one atom to another in their radial parts, from one state to another in their angular parts. The secular determinant is then

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[9] Laporte and Inglis, Phys. Rev. **35**, 1337 (1930).

[10] This is a more detailed formulation of the method of Goudsmit[3] than that given by him.

$$|Av_{ij} + Bw_{ij} - \epsilon\delta_{ij}| = 0. \tag{5}$$

Here A and B are radial integrals, and are considered as parameters that differ among the atoms, while the matrices v_{ij} and w_{ij} are the same for all the atoms considered. (5) may be written

$$\epsilon^N - \epsilon^{N-1}(At_{10} + Bt_{01}) + \epsilon^{N-2}(A^2t_{20} + ABt_{10} + B^2t_{02}) - \cdots = 0. \tag{6}$$

The roots ϵ_k are functions of the parameters A and B. The coefficients t_{kl} are sums of products of v_{pq} and w_{rs}. The integrations involved are to be avoided by determining the coefficients from a knowledge of the energies in extreme couplings.

6. Determination of the coefficients. From consideration of one perturbation at a time, we know the energies near extreme couplings (B/A or A/B small). In (jj) coupling (small B/A) we know the first two coefficients of the Taylor expansion

$$\epsilon_k(A, B) = \alpha_kA + \beta_kB + \cdots, \tag{7.1}$$

the first from the vector model, the second from the calculations of this paper. In (LS) coupling (small A/B) we have similarly

$$\epsilon_k(A, B) = b_kB + a_kA + \cdots. \tag{7.2}$$

Here the coefficients b_k come from the Slater calculation, and express the separation of the multiplets from one another, while a_k constitute the familiar interval rule. In (6) the coefficient of $(-)^n\epsilon^{N-n}$ is the sum of all products of n roots (7.1):

$$\sum_{j=0}^{n} A^{n-j}B^jt_{n-jj} = \sum_{pq\cdots}{}'(\alpha_pA + \beta_pB + \cdots)(\alpha_qA + \beta_qB + \cdots).$$

Assuming convergence of (7.1) for some finite B, we equate the coefficients of the same powers of B. If we know only the first two terms of (7.1), we get only the relations

$$t_{n,0} = \sum_{pq\cdots s}{}'\alpha_p\alpha_q\cdots\alpha_s \qquad (n \text{ factors}) \tag{8.1}$$

$$t_{n-1,1} = \sum_{pq\cdots s}{}'\beta_p\alpha_q\cdots\alpha_s. \quad (n \text{ factors, one of them } \beta) \tag{8.2}$$

An identical treatment of the case of small A/B gives

$$t_{0,n} = \sum_{pq\cdots s}{}'b_pb_q\cdots b_s \qquad (n \text{ factors}) \tag{8.3}$$

$$t_{1,n-1} = \sum_{pq\cdots s}{}'a_pb_q\cdots b_s \quad (n \text{ factors, one of them } a) \tag{8.4}$$

N is the number of states in the set with the same value of J. n has any value from one to N. For $N=3$, (8) are 12 equations. The fact that $t_{1,0}$ and $t_{0,1}$ are determined in each extreme is equivalent to a well-known energy sum rule. For $N>3$, not all the t_{ij} are determined.

7. Example of intermediate coupling, the configuration p^3. This configuration is easily determined both because of its few states and because of the small number of parameters of equivalent electrons. The various levels in extreme couplings, and the corresponding large and small energies, are indicated in Table III. The central level has been selected as reference level.[11]

TABLE III.

	(jj)			(LS)		
J	α	β	J	b	a	
3/2	3	1/3	3/2	2	0	^2P
			1/2	2	0	
1/2	0	2				
5/2	0	0	5/2	0	0	^2D
3/2	0	$-5/3$	3/2	0	0	
3/2	-3	1/3	3/2	-3	0	^4S

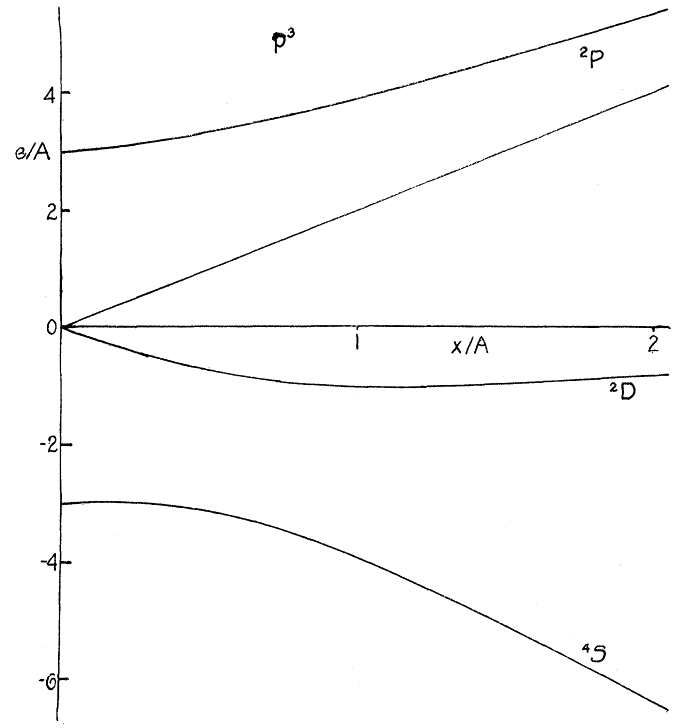

Fig. 2.

Here B = Goudsmit's $X = (3/25)F^2(n1, n1)$. Using Slater's results, b, and the results of the vector model, a, and α, Goudsmit[3] has determined:

$$(jj) : t_{2,0} = -9 \qquad (LS) : t_{0,1} = -1$$

$$t_{1,0} = -1 \qquad t_{0,2} = -6$$

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[11] A linear transformation of the variables ϵ, A, and B, leaves the form of (6) unaltered. Here we subtract from ϵ the energy of the state with $J=5/2$, which is a linear function of A and B.

and the other t's equal to zero, except $t_{2,1}$. Using in addition the values of β in (8.2), we get $t_{2,1}=15$, thus completing the determination of the equation

$$\epsilon^3+\epsilon^2 B-\epsilon(9A^2+6B^2)-15A^2B=0.$$

For the sake of plotting in two dimensions, either A or B is taken as unit of energy, making the levels converge in (jj) or (LS) coupling, respectively, as in Fig. 2 and Fig. 3. In Fig. 3 a comparison of the theory with the experimental data is indicated, in the manner of a previous paper.[9]

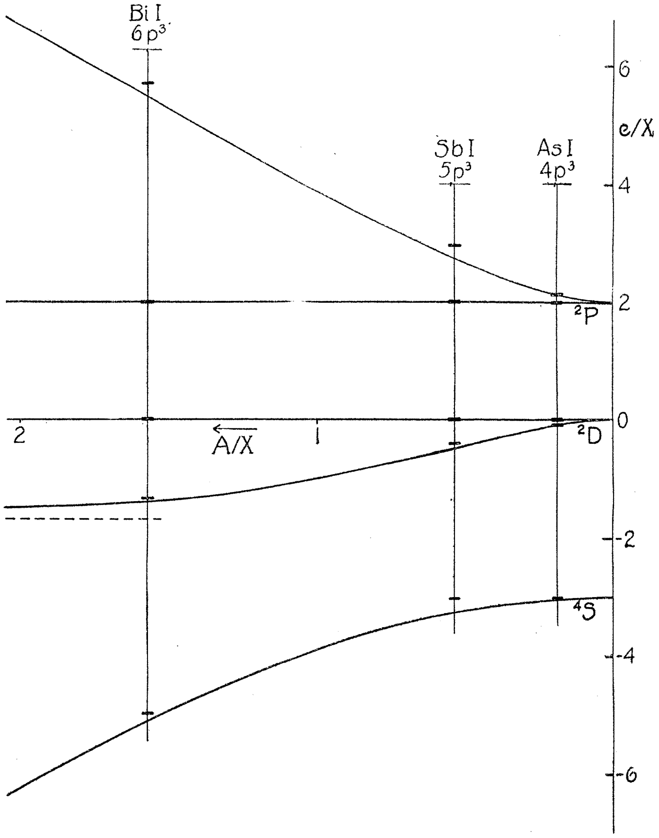

Fig. 3.

Such an extension to intermediate coupling is more difficult for configurations having non-equivalent, non-s-electrons. The first difficulty is introduced by secular equations of higher order, which cannot be treated by this method, but require more direct quantum mechanical methods, involving non-diagonal matrix elements. A second difficulty is that several radial integrals appear as paramaters, so as to render impossible any simple graphical representation of the solutions.

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