Coupling of Electrons with High Orbital Angular Momentum, Illustrated by $2p\ nf$ and $2p\ ng$ in N II

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The theory for intermediate coupling has been studied in the pair-coupling approximation, and is shown to give an accurate description of the observed structure in N II $2s^2\ 2p\ nf$ and N II $2s^2\ 2p\ 5g$.

INTRODUCTION

THERE is a tendency towards pairing of the energy levels when the outer electron assumes high l-quantum numbers, revealing that the spin coupling of this electron has lost most of its significance. Shortley and Fried[1] and Racah[2] have studied this pair coupling in the special case when the electrostatic interaction is small compared to the spin-orbit interaction of the parent ion. This condition is realized in configurations containing almost closed shells, *viz.*,[3] p^5l and d^9l.

The analogous two-electron configurations may illustrate the properties of the pair coupling when there is a considerable electrostatic interaction between levels of different parentage. A good example is furnished by the configurations $2s^2\ 2p\ nf$, $n=4, 5, 6$, and $2s^2\ 2p\ 5g$ in singly ionized nitrogen, which have recently been observed and analyzed in this Laboratory.[4] The observed term structure is shown in Tables III and V.

CONFIGURATION pf

Coupling Integrals

The relative magnitudes of the coupling parameters[5] can be estimated from the spurs of the energy matrices. Since the spurs are independent of the coupling they can be written down directly from the known values of the spin-orbit interaction in jj-coupling[6] and the electrostatic interaction in LS-coupling.[7] The following expressions for the energy levels, $E_J-\bar{E}$, relative to the center of gravity of the configuration, $\bar{E}$, are obtained:

$$\begin{aligned}
E_5-\bar{E} &= \tfrac{1}{2}\zeta_p+5F_2-(75/2)G_2+5G_4+\tfrac{3}{2}\zeta_f,\\
\sum_{E_4}(E_4-\bar{E}) &= -5F_2+(75/2)G_2+9G_4+\zeta_f,\\
\sum_{E_3}(E_3-\bar{E}) &= -\zeta_p-13F_2-18G_2-13G_4-\zeta_f,\\
\sum_{E_2}(E_2-\bar{E}) &= +9F_2+(75/2)G_2+9G_4-\frac{5}{2}\zeta_f,\\
E_1-\bar{E} &= \tfrac{1}{2}\zeta_p+12F_2+(9/2)G_2-30G_4-2\zeta_f.
\end{aligned} \tag{1}$$

Accepting the value for ζ_{2p} obtained from the configuration N II $2s^2\ 2p\ 5g$ (see Table V), the other parameters for the observed N II $2s^2\ 2p\ nf$ configurations are uniquely determined by this set of equations. The results are given in Table I. The contributions of G_4 and ζ_{nf} are not thought to exceed the errors inherent in the theory.

TABLE I. N II $2s^2\ 2p\ nf$ parameter values (cm^{-1}).

n	4	5	6
$\bar{E}$	211 271.55	221 214.51	226 615.69
ζ_{2p}	116.24	116.24	116.24
F_2	13.493	6.927	3.97
G_2	0.262	0.212	0.147
G_4	0.034	0.035	0.029
ζ_{nf}	2.18	1.61	0.95

Energy Levels

It is of interest to study the theoretical structure in the approximation where only the p-electron spin-orbit integral, ζ_p, and the largest electrostatic integral, F_2, are retained. The matrices of electrostatic energy in the LS-scheme[7] can be transformed to the jj-scheme by using the transformation matrices given by Shortley and Fried.[8] After addition of the diagonal spin-orbit interactions[6] one obtains the solution of the secular equation shown in Table II. These formulas represent the pair-coupling approximation in intermediate coupling. The quantum numbers J_p and L have been derived from the limiting cases $F_2/\zeta_p\rightarrow 0$ and $F_2/\zeta_p\rightarrow\infty$.

TABLE II. The energy levels of pf in the pair-coupling approximation.

J	$E-\bar{E}$	J_p	L	K
5, 4	$+\frac{1}{2}\zeta_p+5F_2$	$1\frac{1}{2}$	G	$4\frac{1}{2}$
4, 3	$-\frac{1}{4}\zeta_p-(10/2)F_2\pm\{[\frac{3}{4}\zeta_p-(10/2)F_2]^2+5\times 15F_2^2\}^{\frac{1}{2}}$	$1\frac{1}{2}$	G	$3\frac{1}{2}$
4, 3		$\frac{1}{2}$	F	$3\frac{1}{2}$
3, 2	$-\frac{1}{4}\zeta_p-\frac{3}{2}F_2\mp[(\frac{3}{4}\zeta_p-\frac{3}{2}F_2)^2+12\times 15F_2^2]^{\frac{1}{2}}$	$\frac{1}{2}$	F	$2\frac{1}{2}$
3, 2		$1\frac{1}{2}$	D	$2\frac{1}{2}$
2, 1	$+\frac{1}{2}\zeta_p+12F_2$	$1\frac{1}{2}$	D	$1\frac{1}{2}$

[1] G. H. Shortley and B. Fried, Phys. Rev. **54**, 749 (1938).
[2] G. Racah, Phys. Rev. **61**, 537 (1942); **62**, 438 (1942).
[3] See Ch. E. Moore, *Atomic Energy Levels*, National Bureau of Standards Circular 467 (U. S. Government Printing Office, Washington, D. C., 1949, 1952), for empirical data and references
[4] The experimental details will be published later. $4f$ and part of $5f$ were previously known.[3]
[5] For definitions and notations see E. U. Condon and G. H. Shortley, *Theory of Atomic Spectra* (Cambridge University Press, Cambridge, 1935).
[6] Reference 5, p. 257.
[7] Reference 5, p. 201.
[8] G. H. Shortley and B. Fried, Phys. Rev. **54**, 739 (1938).

TABLE III. N II $2s^2\,2p\,nf$. Observed levels, and differences between observed and calculated centers of gravity of the pairs.

Limit	Designation L	$[K]$	J	$4f$ Obs (cm^{-1})	$4f$ $\langle$Obs$\rangle_{Av}$-calc	$5f$ Obs (cm^{-1})	$5f$ $\langle$Obs$\rangle_{Av}$-calc	$6f$ Obs (cm^{-1})	$6f$ $\langle$Obs$\rangle_{Av}$-calc
$(^2P_{1\frac{1}{2}})$	G	$[4\frac{1}{2}]$	5	211 390.75	±0.0	221 301.90	−0.1	226 689.74	−0.3
			4	211 402.83		221 311.91		226 697.00	
$(^2P_{1\frac{1}{2}})$	G	$[3\frac{1}{2}]$	4	211 295.65	−0.7	221 232.72	−0.4	226 644.05	±0.0
			3	211 288.03		221 227.45		226 641.02	
$(^2P_{\frac{1}{2}})$	F	$[3\frac{1}{2}]$	4	211 061.04	+0.3	221 074.15	+0.1	226 492.89	±0.0
			3	211 057.06		221 070.02		226.489.59	
$(^2P_{\frac{1}{2}})$	F	$[2\frac{1}{2}]$	3	211 030.87	+0.2	221 055.30	+0.2	226 483.48	+0.2
			2	211 033.73		221 057.81		226 485.44	
$(^2P_{1\frac{1}{2}})$	D	$[2\frac{1}{2}]$	3	211 411.27	±0.0	221 293.11	+0.3	226 676.79	+0.3
			2	211 415.96		221 297.04		226.679.20	
$(^2P_{1\frac{1}{2}})$	D	$[1\frac{1}{2}]$	2	211 491.10	+0.4	221 355.27	+0.2	226 721.60	+0.2
			1	211 487.38		221 352.43		226 719.39	
		$\bar{E}$ (cm^{-1})		211 271.55		221 214.51		226 615.69	
		ζ_{2p} (cm^{-1})		116.24		116.24		116.24	
		F_2 (cm^{-1})		13.30		6.78		3.90	
		$\Sigma_E(-1)^J E_J$ (cm^{-1})		35.0		28.7		20.2	

Racah's notation $[K]$ for a pair with $J=K\pm\frac{1}{2}$ is adequate. The interactions between levels of the same quantum number K are represented by the last term, $5\times15F_2{}^2$ and $12\times15F_2{}^2$, respectively, of the radical quantities.

The formulas in Table II have been fitted to the centers of gravity of the observed pairs in N II $2s^2\,2p\,nf$ by taking ζ_{2p} from the analysis of N II $2s^2\,2p\,5g$ (see below) and merely varying F_2. The residuals, given in Table III, are surprisingly small.

The sum of the observed pair splittings may be taken as a kind of measure of the deviation from ideal pair-coupling. In the case of N II $2s^2\,2p\,nf$ the observations show that in each pair the level with odd J-value has the lowest energy. Consequently, the sum of the pair splittings can be written $\sum_E(-1)^J E_J$, or, according to (1),

$$\sum_E(-1)^J E_J = 126G_2 + 56G_4. \qquad (2)$$

This indicates that the deviation from ideal pair-coupling is mainly due to G_2.

The relative arrangement of the energy levels of pf in the pair-coupling approximation is plotted in Fig. 1 as a function of F_2/ζ_p. Superimposed are experimental data for N II $2s^2\,2p\,nf$, $n=4$, 5, 6, and[9] Ne I $2s^2\,2p^5\,4f$. In this approximation the structure of p^5f is identical with that of pf except for the sign of the coefficients of ζ_p and F_2.[10]

TABLE IV. The energy levels of pg in the pair-coupling approximation.

J	$E-\bar{E}$	J_p	L	K
6, 5	$+\frac{1}{2}\zeta_p+28F_2$	$1\frac{1}{2}$	H	$5\frac{1}{2}$
5, 4	$-\frac{1}{4}\zeta_p-(49/2)F_2\pm([\frac{3}{4}\zeta_p-(49/2)F_2]^2+28\times77F_2{}^2)^{\frac{1}{2}}$	$1\frac{1}{2}$	H	$4\frac{1}{2}$
5, 4		$\frac{1}{2}$	G	$4\frac{1}{2}$
4, 3	$-\frac{1}{4}\zeta_p-(22/2)F_2\mp([\frac{3}{4}\zeta_p-(22/2)F_2]^2+55\times77F_2{}^2)^{\frac{1}{2}}$	$\frac{1}{2}$	G	$3\frac{1}{2}$
4, 3		$1\frac{1}{2}$	F	$3\frac{1}{2}$
3, 2	$+\frac{1}{2}\zeta_p+55F_2$	$1\frac{1}{2}$	F	$2\frac{1}{2}$

[9] C. J. Humphreys and H. J. Kostkowski, J. Research Natl. Bur. Standards **49**, 73 (1952).

CONFIGURATION pg

The energy matrix has been calculated in the jj-scheme by using the data given by Shortley and Fried,[8] and the secular equation has been solved in the pair-

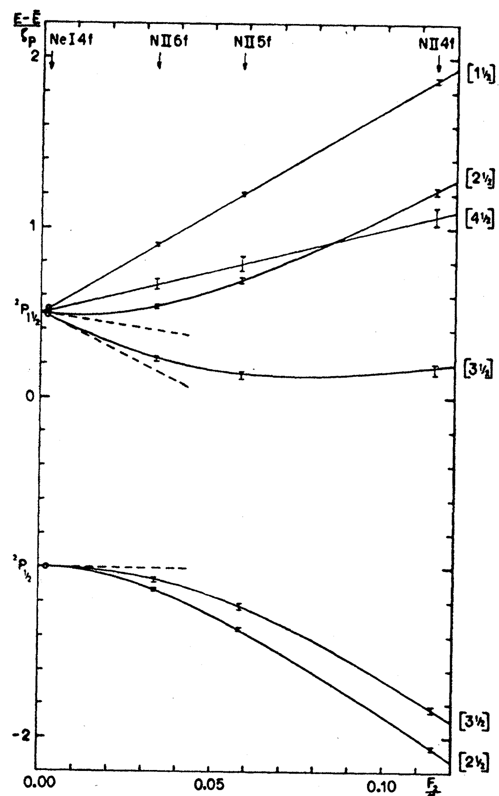

FIG. 1. The structure of pf in pair coupling. (The dashed, straight lines correspond to the approximation obtained by Shortley and Fried by neglecting the interaction between levels of different parentage.)

[10] Reference 5, p. 295.

TABLE V. N II $2s^2\,2p\,5g$. Observed and calculated levels.

Designation				Level (cm^{-1})			
Limit	L	$[K]$	J		Obs	$\langle$Obs$\rangle_{Av}$	Calc
$(^2P_{1\frac{1}{2}})$	H	$[5\frac{1}{2}]$	6, 5	221 364	0.80, 0.78	0.79	0.79
$(^2P_{1\frac{1}{2}})$	H	$[4\frac{1}{2}]$	5, 4	221 323	0.66, 0.56	0.61	0.59
$(^2P_{\frac{1}{2}})$	G	$[4\frac{1}{2}]$	5, 4	221 168	0.37, 0.18	0.29	0.33
$(^2P_{\frac{1}{2}})$	G	$[3\frac{1}{2}]$	4, 3	221 164	0.51, 0.51	0.51	0.51
$(^2P_{1\frac{1}{2}})$	F	$[3\frac{1}{2}]$	4, 3	221 343	0.80, 0.61	0.72	0.70
$(^2P_{1\frac{1}{2}})$	F	$[2\frac{1}{2}]$	3, 2	221 381	···	···	0.08

$\bar{E}=221\,289.792$ cm^{-1}, $\zeta_{2p}=116.237$ cm^{-1}, $F_2=0.6030$ cm^{-1}

coupling approximation with the result shown in Table IV.

The observed N II $2s^2\,2p\,5g$ levels, given in Table V, occur in close pairs with a splitting of less than 0.20 cm^{-1}. The arrangement of the pairs is exactly described by the theoretical formulas. The value $\frac{3}{2}\zeta_{2p}=174.36$ cm^{-1}, derived from this calculation, agrees within experimental errors w tithhe splitting of the ground term $2s^2\,2p\,^2P$ of N III, which is 174.5 cm^{-1} as determined from observations in the extreme ultraviolet.

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Dynamical Theory of Nuclear Induction. II*

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This paper represents the generalization of an earlier theory by Wangsness and the author in which the phenomena of relaxation were treated by considering the interaction of individual nuclear moments with the molecular system and assuming that the latter remains always in thermal equilibrium. Instead of a single nuclear moment, the representative spin system is here allowed to consist of several moments, interacting with each other, and the corresponding general Boltzmann equation for the distribution matrix is developed. A first application is given by investigating the effect of a weak alternating field in the vicinity of resonance conditions. It is seen that the phenomenon of saturation is closely related to the change of populations in states, other than the two between which the resonance transitions occur. This general type of Overhauser effect is shown to be equivalent to that of a dc circuit and it is illustrated by a special example. The general formalism is adapted to the treatment of a nuclear spin system in a strong constant field with particular attention to the structure of resonance spectra in liquids, due to chemical shift and spin coupling. A special case is that where the spin coupling causes a splitting of the lines, large compared to their natural width and their broadening due to the alternating field. An expression for the signal, obtained in this case, is developed and the effect of the spin coupling upon the effective longitudinal and transverse relaxation time is illustrated by the particular example of the two coupled nuclei of spin 1/2 and with independent dipole relaxation. New phenomena appear if the rate of relaxation-transitions is comparable or large compared to the frequency separation of resonance lines, due to spin coupling. The effect of such transitions by some nuclei upon the line width and structure of the resonance of others is investigated, assuming the spin coupling to be small compared to the chemical shift. Similar effects occur to the resonances of a nucleus in a weak alternating field, if other nuclei are at the same time irradiated by an alternating field of different frequency and sufficiently strong so that its effect is comparable or large compared to that of the spin coupling. It is shown that, even for the case of a single kind of nucleus, the presence of the strong field causes a doubling of the resonance with the weak field which can be used to calibrate the strength of the former by a frequency measurement. Another illustration is given in the case of two nuclei and explicit expressions for line width and intensity are given for the example of two nuclei with spin 1/2 and independent dipole relaxation.

1. INTRODUCTION

THE phenomena of nuclear magnetism require the general consideration of a system of nuclear spins, interacting with external fields and with each other. The behavior of the system is further determined by relaxation processes which are due to its interaction with the molecular surroundings. In an earlier paper, referred to below as I, Wangsness and the author[1] have presented a new approach to the problem of relaxation by treating the molecular surroundings as a quantum-mechanical system in thermal equilibrium. Through statistical and perturbation methods they were led to the Boltzmann equation for the distribution matrix which is analogous to the classical distribution function and contains all the information necessary for the description of the spin system.

* Written at CERN, Geneva, during a leave of absence of the author from Stanford University for the academic year 1954–1955.

[1] R. K. Wangsness and F. Bloch, Phys. Rev. 89, 728 (1953).