On the Energy Distribution of Terms and Line Arrays in Atomic Spectra

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The Coulomb interaction leads to a splitting of the different terms belonging to the same many-electron configuration. We have studied the resulting energy distributions of terms and also of line arrays for transitions between different configurations. Expressions are derived for the first two moments of the distributions, namely, the average energy shift and the mean square deviation, as a function of the number of particles. The detailed shapes of the distributions are investigated both for $(d)^n$ configurations and for a simplified two-dimensional model.

§ 1.   Introduction

A problem of great interest in the study of atomic spectra is the splitting between different energy levels due to mutual interactions among electrons. If these interactions could be completely incorporated into the average self-consistent central field, then all terms belonging to the same configuration of one-particle orbitals would be degenerate. If the last shell is partially filled, there are, of course, a number of ways for the electrons to couple their individual angular momenta together. The mutual interactions between them lead to a splitting between the different terms. Terms themselves are subject to further splitting due to the spin-orbit interaction, but we shall not take this effect into account in the present paper.

The resulting energy spectrum is, in general, quite complicated, especially when we can have a large number of particles in the shell. However, under certain simple conditions it is possible to relate the first and second moments (i.e. the average and mean square deviation) of the energy spectrum for an n-particle configuration, $(l)^n$, to those for the basic two-particle configuration $(l)^2$. Since it is usually not too difficult to calculate the level spectrum for a two-particle configuration, we may in this way obtain valuable information concerning the spread of the n-particle spectrum, though, of course, not its detailed structure.[1] We find, for example, that the second moment reaches a maximum for a half-filled shell.

Similar considerations can be applied to the energy distribution of line arrays. In the absence of mutual interactions, the energy of any line will be

just the difference between the single particle energy of the initial and final state for the jumping electron, independent of the coupling between this electron and the others. In the presence of interactions, the energy of any line depends, however, also on the coupling between the jumping electron and the others. The situation can be even more complicated than that for the terms themselves, if both the initial and final states are split by the interactions. In the considerations of this paper we have arbitrarily considered only transitions of the form $l^n \to l^{n-1}l'$ and have further supposed for simplicity that the interaction of the electron in the final state l' with those in the initial state l can be neglected. Even so, the line array distributions are more complicated than are the term distributions in either initial or final state.[2] However, again the average and mean square deviation of the line energy may be related to that for the transition $l^2 \to ll'$.

First, we consider configurations involving identical electrons in the p shell. The distribution of terms and of lines may be calculated using the method of fractional parentage coefficients due to Racah.[3] Relations between first and second moments are explicitly verified in this case. (In Appendix A we present a more general derivation of these relations.) Finally, we treat configurations involving two or three particles in the d shell, interacting via a long-range force. The distribution of levels for the d^3 configuration seems to be very strongly skew, but that for the lines in the transition $d^3 \to d^2l'$ is much less so.

In Appendix B we consider a simple two-dimensional model of interacting particles for which the energies of the individual terms and transition strengths, and thus the detailed shapes of the distributions, can be calculated explicitly.[4] It is found that the distribution of terms is essentially exponential and that of lines is fairly close to a Gaussian.

In Appendix C we derive explicit expressions for the first two moments of the term and line array distributions for two-particle configurations.

§ 2. (p^n) model

A simple example of the considerations discussed in this paper is provided by the following model: We consider a number of identical spin 1/2 particles in a p shell ($l=1$) interacting via central, spin independent interactions. Because of the Pauli principle, we can put no more than six particles into this shell. If we have two particles in this shell, the possible terms are ^1S, ^3P, ^1D. In the absence of mutual interactions these three terms are degenerate. The interaction splits these. We denote the energies by s, p, and d, respectively. However, unless there is spin-orbit coupling, there is no further splitting, say, between the $^3P_0$, $^3P_1$, and $^3P_2$ levels. Now, for this case the average energy of the p^2 configuration with each term weighed by the appropriate statistical factor $(2S+1)(2L+1)$ is given by

$$E_{av} = \frac{1}{15}[s + 9p + 5d]. \tag{2.1}$$

A measure of the spread of the terms is provided by the mean square deviation $\Delta^2 E$

$$\Delta^2 E = E^2_{av} - (E_{av})^2 = \frac{2}{225}[7s^2 + 27p^2 + 25d^2 - 9sp - 5sd - 45pd]. \tag{2.2}$$

Now suppose we put three particles into the shell. Again there are three possible states: ^4S, ^2P, ^2D. The energy levels for the p^3 configuration can be expressed directly in terms of those for the p^2 configuration using the method of fractional parentage coefficients (*fpc*) due to Racah.[3]

Thus, we obtain

$$E(^4S) = 3p,$$

$$E(^2P) = \frac{2}{3}s + \frac{3}{2}p + \frac{5}{6}d, \tag{2.3}$$

$$E(^2D) = \frac{3}{2}p + \frac{3}{2}d.$$

It may be seen that

$$E_{av}(p^3) = 3E_{av}(p^2),$$

$$\Delta^2 E(p^3) = \frac{3}{2}(\Delta^2 E)(p^2), \tag{2.4}$$

regardless of the specific values of the energies. We can similarly calculate the energy of states in the p^4 configuration. This is just a mirror of the p^2 configuration and (apart from a constant displacement) the energy levels are the same as that for p^2. Thus, we find

$$E(p^4)_\alpha = E(p^2)_\alpha + 5E_{av}(p^2),$$

$$E_{av}(p^4) = 6E_{av}(p^2), \tag{2.5}$$

$$\Delta^2 E(p^4) = \Delta^2 E(p^2).$$

The above regularities suggest that there are some simple rules relating the first and second moments of the multiplet energy spectra.

A similar type of regularity seems also to occur for the spectral distribution of lines. Consider, for example, the two-particle line array $p^2 \rightarrow pl'$. Here an electron jumps from the p shell to some other shell l', where its interaction with p electrons can be ignored. In this case the pl' levels are degenerate, and thus each component of the line has the same energy (except for a constant displacement) as the p^2 configuration. It does not matter what the state l' is. Consequently, we find that E_{av} and $\Delta^2 E$ for the $p^2 \rightarrow pl'$ lines are the same

as that for the p^2 configuration itself. Now, for the $p^3 \rightarrow p^2 l'$ lines the situation is more complicated. In this case, the line spectrum depends not only on the level splitting of both initial and final configurations, but also on the intensity of each line between the various multiplets. However, the line spectrum may be readily calculated by means of the method of *fpc*.

Table I.

Energies and strengths of lines in $p^3 \rightarrow p^2 l'$ transition.

		^1S	^3P	^1D
p^3	^4S	$-s+3p,\ 0$	$2p,\ 4$	$-d+3p,\ 0$
	^2P	$-(1/3)s+(3/2)p+(5/6)d,\ 4/3$	$(2/3)s+(1/2)p+(5/6)d,\ 3$	$(2/3)s+(3/2)p-(1/6)d,\ 5/3$
	^2D	$-s+(3/2)p+(3/2)d,\ 0$	$(1/2)p+(3/2)d,\ 5$	$(3/2)p+(1/2)d,\ 5$

In this case, the strength of each line is independent of the nature of the mutual interactions, only the energy depends on the interaction. One finds that

$$E_{av}(p^3 \rightarrow p^2 l') = 2E_{av}(p^2 \rightarrow p l') . \tag{2.6}$$

E refers, of course, to the energy *shift*, the displacement of the line with respect to that of the single particle line $p \rightarrow l'$. The mean square deviation $\Delta^2 E$ given by

$$\Delta^2 E(p^3 \rightarrow p^2 l') = (3/2)\,\Delta^2 E(p^2 \rightarrow p l'). \tag{2.7}$$

Thus, again the first and second moments are simple multiples of those for the is two-particle case.

§ 3. General relations among first and second moments of distributions

Similar calculations were also made for a number of other kinds of configurations, for example, d^n (cf. § 4), and we always obtain regularities similar to those for the p^n shell mentioned above. The important parameters seem to be (a) the maximum number of particles which can go into the shell and (b) the actual number of particles in the shell. The detailed value of the angular momentum seems to be important only insofar as it determines the number of available sub-states in the shell. Quite generally, we find that the average energies for the n-particle case are related to those for the two-particle case by[1]

$$E_{av}(l^n) = \frac{n(n-1)}{2}\,E_{av}(l^2) , \tag{3.1}$$

$$E_{av}(l^n \rightarrow l^{n-1}\,l') = (n-1)\,E_{av}(l^2 \rightarrow l l'). \tag{3.2}$$

Regarding the mean square fluctuation $\Delta^2 E$ of the energy, there are similar general regularities. If we neglect the anti-symmetry requirement on the wave function, i.e. if we assume that we can put an infinite number of particles into each sub-

state and do not attempt to anti-symmetrize the wave function, then one finds that

$$\Delta^2 E(l^n) = \frac{n(n-1)}{2} \Delta^2 E(l^2), \qquad (3\cdot3)$$

$$\Delta^2 E(l^n \to l^{n-1} l') = (n-1) \Delta^2 E(l^2 \to ll'). \qquad (3\cdot4)$$

On the other hand, if we consider equivalent particles, for which we can only put N_0 into a shell, we then obtain instead

$$\Delta^2 E(l^n) = \frac{n(n-1)(N_0-n)(N_0-n-1)}{2(N_0-2)(N_0-3)} \Delta^2 E(l^2), \qquad (3\cdot5)$$

$$\Delta^2 E(l^n \to l^{n-1} l') = \frac{(n-1)(N_0-n)}{(N_0-2)} \Delta^2 E(l^2 \to ll'). \qquad (3\cdot6)$$

These rules have been verified even when we consider configuration interaction between two different levels. In particular, in one case where we have a $j=3/2$ and a $j=1/2$ level, with configuration between them, the above rule also holds provided only that the *average* interaction energy of a particle with the others is independent of its sub-state. This is clearly true in any given j shell due to spherical symmetry. It is also true in a mixed shell if the two levels are degenerate in the central field approximation. A more general derivation of these rules is given in Appendix A. Note that in considering a line array such as $p^3 \to p^2 l'$, the interactions among the non-jumping electrons are the same in both initial and final state. These tend to cancel out in the determination of the line spread and consequently the line spread is smaller than the spread of the p^3 configuration itself.

We have also investigated second moments for more complicated lines taking into account interactions between electrons in initial and final state. Thus, consider the line array

$$l_1{}^{n_1} l_2{}^{n_2-1} \to l_1{}^{n_1-1} l_2{}^{n_2}.$$

In this case, the second moments appear to be given by

$$\Delta^2 E = \frac{(n_1-1)(N_1-n_1)}{(N_1-2)} \Delta^2 E(l_1{}^2 \to l_1 l_2) + \frac{(n_2-1)(N_2-n_2)}{(N_2-2)} \Delta^2 E(l_1 l_2 \to l_2{}^2) \quad (3\cdot7)$$

where N_1 and N_2 denote maximum occupation numbers of orbits l_1 and l_2. However, this relation has been verified only for some simple examples and has not been proven in general.

Another example is the array

$$l_1 \, l_3{}^n \to l_2 \, l_3{}^n$$

for which case it appears that

$$\Delta^2 E = \frac{n(N_3-n)}{(N_3-1)} \Delta^2 E(l_1 \, l_3 \to l_2 \, l_3). \qquad (3\cdot8)$$
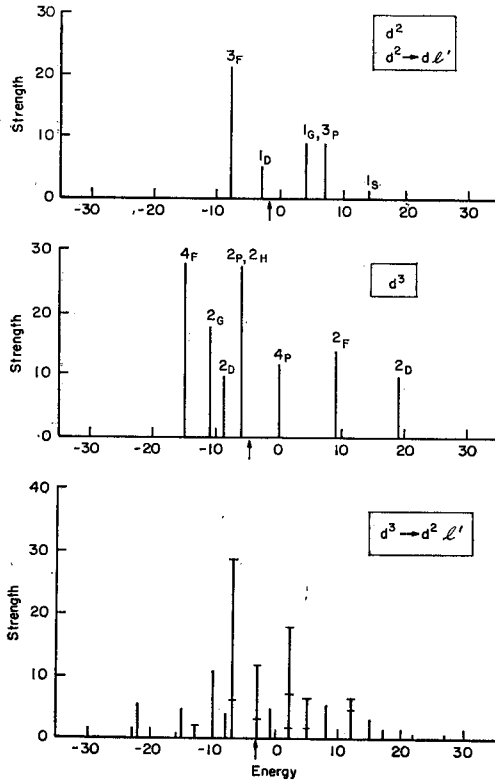
§ 4. d^n model

Fig. 1. Spectra for d^2 and d^3 levels and for $d^2 \rightarrow dl'$ and $d^3 \rightarrow d^2 l'$ lines, assuming P_2 (cos θ) interaction. Arrows indicate mean energies.

A somewhat more complicated example is provided by the following model: We assume that there are a number of particles in the d shell ($l=2$) subject to mutual interactions of the form $P_2(\cos \theta_{ik})$. This is a good approximation for long-range forces, such as the Coulomb forces, between electrons.[5]

We consider three cases. First, the spectrum of the terms of the d^2 configuration. This is the same as that for the $d^2 \rightarrow dl'$ lines. (The particles in the final state l' are assumed not to interact with the ones in the d shell.) The second case we consider is the spectrum of the levels for the d^3 configuration. The energy levels for the d^2 and d^3 configurations have been given by Racah.[3] The statistical weight of each term is, of course, $(2S+1)(2L+1)$. Finally, the calculation of the $d^3 \rightarrow d^2 l'$ line spectrum is somewhat more complicated. Thus, it requires knowledge of the properties of both the initial and final states. However, the line spetrum may be calculated without too much trouble, again using the method of fractional parentage coefficients. The energy levels and lines are plotted in Fig. 1 according to the energy and the strength. The first three moments are also listed in the following table.

Table II.

Moments of distributions for d^2 and d^3 levels and for $d^3 \rightarrow d^2 l'$ lines assuming P_2 (cos θ) interaction. (Energies are expressed in units of the parameter, B, defined by Racah.[6] The other parameters, A and C, vanish in this case.)

Case	E_{av}	$(\Delta^2 E)$	$(\Delta^3 E)/(\Delta^2 E)^{3/2}$
d^2, $d^2 \rightarrow dl'$	−1.556	45.80	0.380
d^3	−4.667	103.05	1.048
Ratio d^3/d^2	3	2.25	2.758
$d^3 \rightarrow d^2 l'$	−3.111	80.15	0.173
Ratio $d^3 \rightarrow d^2 l'/d^2 \rightarrow dl'$	2	1.75	0.455

The relation between these moments bears out the results of § 2–b. It is seen that the spectrum of d^2 is skew and that of d^3 even more strongly so. All the really strong levels are at the low energy end. As we shall see in Appendix B, for many particles in the shell, the term distribution should have a strongly skew exponential shape. The amount of skewness is characterized by the ratio $(\varDelta^3 E)/(\varDelta^2 E)^{3/2}$. However, the line spectrum for $d^3 \to d^2 l'$ is nearly symmetric about its mean; thus the skewness parameter is much smaller for this case. We would expect that for a more complicated configuration the skewness might be-
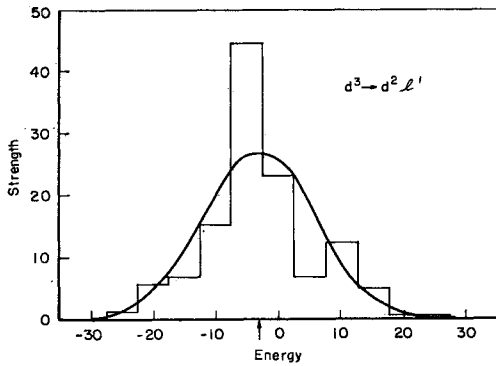

come even smaller. For the simple two-dimensional model of particles discussed in Appendix B, the line shape is in fact symmetric in the limit of a very large number of particles. Another parameter of interest, which characterizes the shape of the symmetric distribution, is the ratio $(\varDelta^4 E)/(\varDelta^2 E)^2$. For the line $d^3 \to d^2 l'$, this ratio equals about 2.55, quite close to the value 3 appropriate to a Gaussian distribution.

Fig. 2. Histogram of spectrum for $d^3 \to d^2 l'$ line, assuming $P_2(\cos\theta)$ interaction. Also shown for comparison is a Gaussian Distribution with the same $\overline{E}$ and $\varDelta^2 E$. Arrow indicates mean energy.

Figure 2 shows a histogram which indicates the near symmetry of the $d^3 \to d^2 l'$ line distribution. Also sketched for comparison is the Gaussian distribution with the same value of E_{av} and $(\varDelta^2 E)$. It is seen to give a fairly good fit to the correct distribution.

Appendix A

General calculation of $\varDelta^2 E$ for term and line array distributions

The mean square deviation of the term and line array distributions can be calculated generally under certain simplifying assumptions. According to the method of second quantization, the interaction hamiltonian can be written as follows:

$$H = \frac{1}{2} \sum_{ijkl} v_{ij \to kl}\, a_k{}^*\, a_l{}^*\, a_j\, a_i \tag{A·1}$$

where $v_{ij \to kl}$ refers to a matrix element of the interaction leading to scattering of a pair of particles from states ij to kl, and $a_i,\, a_k{}^*$ refer to annihilation and and creation operators, respectively. The latter obey the well-known commutation rules for Fermions:

$$a_i\, a_k + a_k\, a_i = 0,$$

$$a_i\, a_k{}^* + a_k{}^*\, a_i = \delta_{ik}, \tag{A·2}$$

$$a_i^* a_k^* + a_k^* a_i^* = 0.$$

Evidently, terms with $i = j$ or $k = l$ do not contribute to the energy. In fact, we can write

$$H = \sum_{i<j} \sum_{k<l} u_{ij \to kl} a_k^* a_l^* a_j a_i \qquad (A \cdot 3)$$

where

$$u_{ij \to kl} = v_{ij \to kl} - v_{ij \to lk}.$$

For the sake of simplicity, we now suppose that only those matrix elements are finite for which both k and l are different from ij, i.e. for which all four indices $ijkl$ are different. This implies that all diagonal elements, e.g. $u_{ij \to ij}$, and also terms in which one particle changes its state, e.g. $u_{ij} \to u_{ik}$, are assumed to vanish.

These conditions are not actually satisfied for the l^n configurations, since some diagonal elements are finite. However, it has been shown by more detailed calculations that our conclusions will still hold provided we have

$$\sum_i u_{ij \to ik} = \text{const} \times \delta_{jk} \qquad (A \cdot 4)$$

where $\delta_{jk} = 1$ if $j = k$,
$\qquad\qquad 0 \quad\; j \neq k$.

The latter condition holds for l^n configurations. If $j \neq k$, all terms in the series are off-diagonal, involving the change of state of one particle. For pure configurations, these must vanish from elementary angular momentum considerations. If $j = k$, we have the sum $\sum u_{ij \to ij'}$, i.e. the average interaction of a particle with those in other states; this quantity must be independent of the sub-state j as discussed in the text.

According to our more drastic assumptions, the average interaction energy E_{av}, which is a linear combination of diagonal elements, must vanish. Thus, we must have $\Delta^2 E = E^2_{av}$. Now, we can use the rule of traces to calculate the second moment. In general, the average $\langle f(E) \rangle_{av}$ of a polynominal function f is given by

$$\langle f(E) \rangle_{av} = \frac{\text{Tr} f(H)}{\text{Tr}(1)} \qquad (A \cdot 5)$$

where Tr refers to the trace.

In particular,

$$\langle E^2 \rangle_{av} = \frac{\text{Tr}(H^2)}{\text{Tr}(1)}. \qquad (A \cdot 6)$$

Now
$$\text{Tr}(1) = N = \binom{N_0}{n} = \frac{N_0!}{n! (N_0 - n)!} \qquad (A \cdot 7)$$

where N is the total number of product states for the l^n configuration. The numerator is given as follows:

$$\mathrm{Tr}\,(H^2) = \mathrm{Tr}\Big(\sum_{i<j}\sum_{k<l} u_{ij\to kl}\, a_k{}^*\, a_l{}^*\, a_j\, a_i\Big)^2 \tag{A·8}$$

$$= \mathrm{Tr}\sum_{i<j}\sum_{k<l}\sum_{i'<j'}\sum_{k'<l'} u_{ij\to kl}\, u_{k'l'\to i'j'}$$

$$\times a_{i'}{}^*\, a_{j'}{}^*\, a_{l'}\, a_{k'}\, a_k{}^*\, a_l{}^*\, a_j\, a_i$$

(we suppose that the matrix elements of u are real). Now the trace vanishes unless each a_i is accompanied by an $a_i{}^*$.

Thus we obtain

$$\mathrm{Tr}\sum_{i<j}\sum_{k<l}(u_{ij\to kl})^2 a_i{}^*\, a_j{}^*\, a_l\, a_k\, a_k{}^*\, a_l{}^*\, a_j\, a_i. \tag{A·9}$$

With the help of the commutation relations, this can be rearranged to read:

$$\mathrm{Tr}\sum_{i<j}\sum_{k<l}(u_{ij\to kl})^2\, a_j{}^*\, a_j\, a_i{}^*\, a_i\, a_k\, a_k{}^*\, a_l\, a_l{}^*. \tag{A·10}$$

Now $a_i{}^* a_i = N_i = 1$ or 0 according to whether state i is occupied or empty. Thus

$$\mathrm{Tr}\,(H^2) = \sum_{i<j}\sum_{k<l}(u_{ij\to kl})^2 N_j\, N_i\,(1-N_k)\,(1-N_l) \tag{A·11}$$

$$= \sum_{i<j}\sum_{k<l}(u_{ij\to kl})^2 N_{ij(kl)}.$$

Here $N_{ij(kl)}$ denotes the number of product states of the l^n configuration with ij full and kl empty, i.e. the number of product states obtained by arranging the remaining $n-2$ particles among the N_0 orbits other than $ijkl$.

We find

$$N_{ij(kl)} = \binom{N_0-4}{n-2} \tag{A·12}$$

and finally

$$\Delta^2 E(l^n) = \sum_{i<j}\sum_{k<l}(u_{ij\to kl})^2\frac{N_{ij(kl)}}{N} = \sum_{i<j}\sum_{k<l}(u_{ij\to kl})^2 \tag{A·13}$$

$$\times\frac{n(n-1)(N_0-n)(N_0-n-1)}{(N_0)(N_0-1)(N_0-2)(N_0-3)} = \frac{n(n-1)}{2}\frac{(N_0-n)(N_0-n-1)}{(N_0-2)(N_0-3)}\Delta^2 E(l^2)$$

in agreement with the result given in the text.

Next, we calculate $\Delta^2 E$ for the array of $l^n \to l^{n-1} l'$ lines, neglecting the interaction of electrons in state l' with those in state l. For the purpose of our discussions, we can ignore the presence of electron l', i.e. consider only those in state l.

Suppose the electron jumps from a sub-state denoted by q. Then the final state can be represented by

$$\psi_f(l^{n-1}) = a_q\,\psi_i(l^n). \tag{A·14}$$

As before, since we suppose that all diagonal elements of the interaction vanish, so does the average displacement of the line array.

The second moment is given by

$$\Delta^2 E = \langle E^2 \rangle_{av} = \left[(E_i - E_f)^2 \right]_{av} = (E_i^2 - 2E_i E_f + E_f^2)_{av} . \qquad (A \cdot 15)$$

Now
$$\langle E_i^2 \rangle_{av} = \mathrm{Tr}\,(H^2 a_q^* a_q) / \mathrm{Tr}\,(a_q^* a_q) . \qquad (A \cdot 16)$$

But
$$\mathrm{Tr}\,(a_q^* a_q) = N\,(n/N_0) \equiv M.$$

(Only terms where sub-state q is occupied can contribute to the line.) The trace is taken with respect to the states of the l^n configuration, and N denotes the total possible number of lines.

Similarly

$$\langle E_f^2 \rangle_{av} = \mathrm{Tr}\,(a_q^* H^2 a_q) / M \qquad (A \cdot 17)$$

and

$$\langle E_i E_f \rangle_{av} = \mathrm{Tr}\,(H a_q^* H a_q) / M. \qquad (A \cdot 18)$$

Thus

$$\Delta^2 E = \mathrm{Tr}\,(H^2 a_q^* a_q - 2 H a_q^* H a_q + a_q^* H^2 a_q) / M. \qquad (A \cdot 19)$$

Now

$$\mathrm{Tr}\,(H^2 a_q^* a_q) = \mathrm{Tr} \sum_{i<j,\ k<l} (u_{ij \to kl})^2 \qquad (A \cdot 20)$$
$$\times a_i^* a_j^* a_l a_k a_k^* a_l^* a_j a_i a_q^* a_q .$$

$$\mathrm{Tr}\,(H a_q^* H a_q) = \mathrm{Tr} \sum_{i<j,\ k<l} (u_{ij \to kl})^2 \qquad (A \cdot 21)$$
$$\times a_i^* a_j^* a_l a_k a_q a_k^* a_l^* a_j a_i a_q .$$

$$\mathrm{Tr}\,(a_q^* H^2 a_q) = \mathrm{Tr} \sum_{i<j} \sum_{k<l} (u_{ij \to kl})^2 \qquad (A \cdot 22)$$
$$\times a_q^* a_i^* a_j^* a_l a_k a_k^* a_l^* a_j a_i a_q .$$

If none of *ijkl* equals q, the three traces are equal, and we obtain no net contribution to $\Delta^2 E$. Suppose, however, that $j = q$. Then the sequence of creation and annihilation operators in the first trace is

$$a_i^* a_q^* a_l a_k a_k^* a_l^* a_q a_i a_q^* a_q \qquad (A \cdot 23)$$
$$= a_i^* a_i a_k a_k^* a_l a_l^* a_q^* a_q = N_{iq(kl)}.$$

On the other hand, the second and third traces vanish, since any sequence including two a_q operators without an a_q^* in between must vanish. The contribution of the terms with $j = q$ to $\Delta^2 E$ is thus given by

$$\Delta^2 E_{(j=q)} = \sum_{i<q} \sum_{kl} (u_{iq \to kl})^2 \frac{N_{iq(kl)}}{M} = \sum_{i<q} \sum_{kl} (u_{iq \to kl})^2$$

$$\times \frac{(n-1)\,(N_0-n)\,(N_0-n-1)}{(N_0-1)\,(N_0-2)\,(N_0-3)} \; . \tag{A$\cdot$24}$$

For $i=q$ we obtain a similar contribution except that the sum involves

$$\sum_{j>q}\sum_{kl}(u_{qj\to kl})^2 \tag{A$\cdot$25}$$

which, by a change of indices, equals

$$\sum_{i>q}\sum_{kl}(u_{qj\to kl})^2 \; . \tag{A$\cdot$26}$$

On the other hand, if $k=q$, the first two traces vanish and the third trace gives the sequence

$$a_q{}^* a_i{}^* a_j{}^* a_i a_q a_q{}^* a_i{}^* a_j a_i a_q \tag{A$\cdot$27}$$

$$= a_i{}^* a_i a_j{}^* a_j a_i a_i{}^* a_q{}^* a_q = N_{ijq(l)} = \binom{N_0-4}{n-3}$$

with a contribution to $\varDelta^2 E$ given by

$$\varDelta^2 E_{(k=q)} = \sum_{ij}\sum_{l>q}(u_{ij\to ql})^2 \frac{N_{ijq(l)}}{M} \tag{A$\cdot$28}$$

$$= \sum_{ij}\sum_{q<l}(u_{ij\to ql})^2 \frac{(n-1)\,(n-2)\,(N_0-n)}{(N_0-1)\,(N_0-2)\,(N_0-3)} \; .$$

The term with $l=q$ gives a contribution of the same form except that the inequality sign is reversed.

Making a change of indices $i\leftrightarrow l$, $j\leftrightarrow k$, we find that

$$(u_{ij\to ql})^2 \to (u_{lk\to qi})^2 = (u_{iq\to kl})^2 \; . \tag{A$\cdot$29}$$

Combining the four contributions to $\varDelta^2 E$, we finally obtain

$$\varDelta^2 E = \sum_i \sum_{k<l}(u_{iq\to kl})^2 \frac{(n-1)\,(N_0-n)}{(N_0-1)\,(N_0-2)} \tag{A$\cdot$30}$$

$$= \frac{(n-1)\,(N_0-n)}{(N_0-2)} \varDelta^2 E(l^2 \to ll') \; ,$$

the same result as given in the text.

Appendix B

System of interacting particles in two-dimensional p shell

It is of interest to consider a simple model of interacting particles for which the term and line distributions can be calculated explicitly, even when there are many particles involved. Such a model is provided by a set of non-equivalent (distinguishable) particles in the two-dimensional version of a p shell.

In this shell there are only two different spatial wave functions. The dis-

tinguishability of the particles implies that there is no restriction on the number of particles in each state, an assumption which greatly simplifies our calculations.

It can be readily shown that this system is equivalent to a system of spin 1/2 particles in an ordinary three-dimensional space. Any interaction of the form: $\beta \cos 2(\theta_i - \theta_k)$ between the p-shell particles gives the same matrix elements as

$$\beta[s_x(i) \cdot s_x(k) + s_y(i) \cdot s_y(k)] = \beta[s(i) \cdot s(k) - s_z(i) \cdot s_z(k)] \qquad (B \cdot 1)$$

between the spin 1/2 particles.

Even in a many-particle configuration, this interaction will leave both the total spin S and its z-component S_z a good quantum number.

For an n-particle configuration, S and S_z can take all integral or half-integral values up to $(1/2)n$, depending on whether n is even or odd. We will, however, suppose that $n \gg 1$, so that both S and S_z may be treated as continuous variables. Using the vector model, it is readily shown that the energy levels are given by

$$E(n, S, S_z) = \frac{1}{2}\beta(S(S+1) - S_z{}^2 - \frac{1}{2}n) \xrightarrow[n \to \infty]{} \frac{1}{2}\beta(S^2 - S_z{}^2). \qquad (B \cdot 2)$$

Of course, there are many different states with the same S and S_z and these states will remain degenerate under the influence of the above interaction.

In order to obtain the energy spectrum of the levels, we must know what fraction of the levels have a given S and S_z.

This is readily shown to equal

$$f(S, S_z) = \sqrt{\frac{32}{\pi n^3}} S \exp\left(\frac{-2S^2}{n}\right) \text{ if } |S_z| \leq S,$$

$$0 \qquad\qquad\qquad \text{if } |S_z| > S. \qquad (B \cdot 3)$$

The distribution of levels may be expressed in the form

$$P(E) = \int_0^\infty \int_{-S}^{S} f(S, S_z) \delta[E - \frac{1}{2}\beta(S^2 - S_z{}^2)] dS_z dS. \qquad (B \cdot 4)$$

Carrying out the integrations we obtain

$$P(E) = \frac{4}{n\beta} \exp\left(-\frac{4E}{n\beta}\right) \quad E > 0,$$

$$0 \qquad\qquad E < 0. \qquad (B \cdot 5)$$

For the simplified example considered here, the distribution of levels is exponential. A tendency toward this kind of distribution was already noted in §4 for the case of a d^3 configuration.

The situation is slightly more complicated in the case of lines. Consider a transition of the form

$$p^n \to p^{n-1}l'$$

where the particle in state l' is assumed not to interact with those in the state p. It is then just as if one of the original particles in the p shell had·simply disappeared. Thus, the final state may be characterized by the configuration of the remaining $n-1$ particles in the p shell. In the transition, S and S_z may each increase or decrease by $1/2$. Thus the line strength function may be expressed as follows:

$$I(E) = \sum_{S'=S\pm1/2} \sum_{S_z'=S_z\pm1/2} \int_0^\infty W(S, S_z \to S', S_z')$$

$$\times f(S, S_z)\, \delta[E - E(S, S_z \to S', S_z')]\, dS_z dS, \qquad \text{(B·6)}$$

where E denotes the energy of a given line, and W is a comparative line intensity normalized such that

$$\sum_{S'} \sum_{S_z'} W(S, S_z \to S', S_z') = 1. \qquad \text{(B·7)}$$

These line intensities may be calculated by use of elementary sum rules. Thus we obtain

$$W(S, S_z \to S', S_z') = \frac{1}{4S}(S \pm S_z) \qquad \text{(B·8)}$$

where the $+$ or $-$ sign applies depending on whether S and S_z change in the same or in opposite directions.
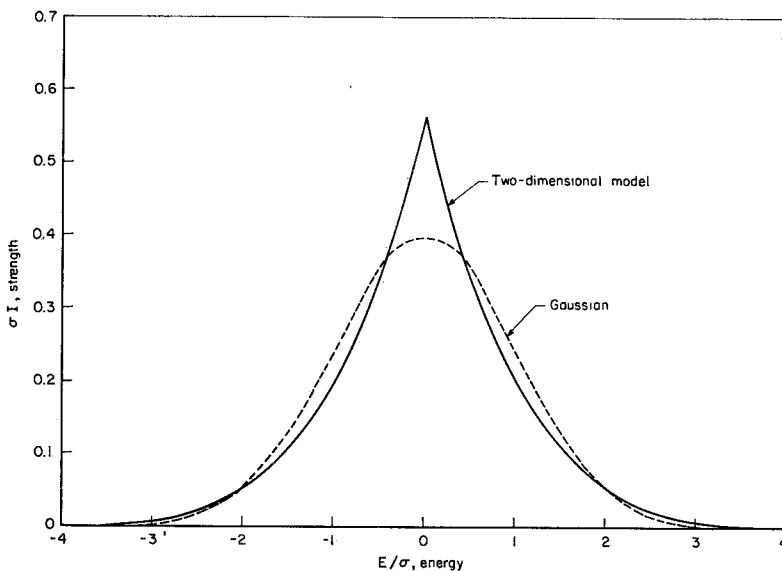
From (B·2) we see that

Fig. 3. Line strength function for interacting particles in two-dimensional p-shell compared to Gaussian distribution with same mean square deviation.

$$E(S, S_z \rightarrow S', S_z') = \beta (S - S' - S_z + S_z').$$ (B·9)

Substituting the last two equations into (B·6), it follows by a series of elementary integrations that

$$I(E) = \sqrt{\frac{8}{\pi n \beta^2}} \exp\left(-\frac{2E^2}{n\beta^2}\right) - \frac{4|E|}{n\beta^2} \mathrm{Erfc}\left(\sqrt{\frac{2E^2}{n\beta^2}}\right).$$ (B·10)

This function agrees fairly closely with a Gaussian of the same mean square deviation $1/8 \cdot n\beta^2$ as is indicated in Fig. 3. We have already noted that the distribution of lines in the $d^3 \rightarrow d^2 l'$ transition resembles a Gaussian. In any case, the line distribution, unlike the level distribution is symmetric about its center, and both distributions fall off sharply far away from the center.

Appendix C

Moments of distributions for two-particle configurations

In this Appendix we derive explicit expressions for the first two moments of the term and line array distributions for two-particle configurations.[7]

Consider first the following simple case. We have two identical spin 1/2 particles in states of angular momentum j and j' coupling to a total angular momentum J. (Assume the validity of j-j coupling.) The two-particle interaction energy is given by

$$E(j_1 j_2 J) = \sum_k (f_k F^k - g_k G^k)$$ (C·1)

where F^k and G^k are well-known Slater integrals. The quantities f_k and g_k can, in turn, be expressed as follows:

$$f_k = a_k A^k$$ (C·2)

$$g_k = b_k B^k$$

$$a_k(j_1 j_2 J) = [(2j_1+1)(2j_2+1)]^{1/2} (-1)^{j_1+j_2-J}$$ (C·3a)

$$\times W(j_1 j_2 j_1 j_2, Jk),$$

$$b_k(j_1 j_2 J) = [(2j_1+1)(2j_2+1)]^{1/2} W(j_1 j_2 j_2 j_1, Jk).$$ (C·3b)

W denotes a Racah coefficient.

In principle, the sum in (C·1) extends over all k. However, from well-known properties of the Racah coefficients, it follows that a_k can be nonvanishing only if $k \leq \min$ of $(2j_1, 2j_2)$ and that b_k vanishes unless $|j_1 - j_2| \leq k \leq j_1 + j_2$.

$$A_k = [(2j_1+1)(2j_2+1)]^{-1/2} \langle j_1 \| c^k \| j_1 \rangle \langle j_2 \| c^k \| j_2 \rangle,$$ (C·4a)

$$B_k = [(2j_1+1)(2j_2+1)]^{-1/2} \langle j_1 \| c^k \| j_2 \rangle^2.$$ (C·4b)

The reduced matrix element $\langle j_1 \| c^k \| j_2 \rangle$ is defined by

$$\langle j_1 m_1 | c_k{}^\mu | j_2 m_2 \rangle = (2j_1+1)^{-1/2} \langle j_1 \| c^k \| j_2 \rangle (j_2 m_2 k \mu | j_1 m_1)$$ (C·5)

where

$$c_k{}^\mu = [4\pi/(2k+1)]^{1/2} Y_k{}^\mu ,$$

and $(\ |\ )$ denotes a Clebsch-Gordan coefficient.

We have

$$\langle j_1 \| c^k \| j_2 \rangle = (-1)^{j_1+j_2-1}(2j_1+1)^{1/2}(j_1\,1/2\,k0|\,j_2\,1/2) \qquad (C\cdot 6)$$

independent of the values of the orbital angular momenta l_1 and l_2, provided only that $l_1 + l_2 + k$ is even. If $l_1 + l_2 + k$ is odd, the matrix element vanishes. We have expressed the energy in this fashion, since now only a_k and b_k depend on J. Thus, the average energy of the configuration (averaged over J) is given by

$$\langle E(j_1 j_2 J)\rangle_{av(J)} = \sum_k [\langle a_k(j_1 j_2 J)\rangle_{av(J)} A_k F^k \qquad (C\cdot 7)$$

$$- \langle b_k(j_1 j_2 J)\rangle_{av(J)} B_k G^k] .$$

The average value of any quantity $Q(J)$ over the configuration is defined by:

$$\langle Q(J)\rangle_{av(J)} = \sum_J (2J+1) Q(J) / \sum_J (2J+1) \quad |j_1-j_2| \le J \le j_1+j_2 . \quad (C\cdot 8)$$

Thus the average of a_k and b_k may be calculated explicitly using well-known sum rules for Racah coefficients.[7] We obtain

$$\langle a_k(j_1 j_2 J)\rangle_{av(J)} = \delta_{k0} , \qquad (C\cdot 9a)$$

$$\langle b_k(j_1 j_2 J)\rangle_{av(J)} = [(2j_1+1)(2j_2+1)]^{-1/2} . \qquad (C\cdot 9b)$$

It is also seen that $A_0 = 1$. Thus the average energy is given by

$$\langle E(j_1 j_2 J)\rangle_{av(J)} = F^0 - [(2j_1+1)(2j_2+1)]^{-1/2} \sum_k B_k G^k . \qquad (C\cdot 10)$$

We can use the same method to calculate the average value of E^2, and find the following result:

$$\langle E^2(j_1 j_2 J)\rangle_{av(J)} = \sum_k \sum_{k'} [\langle a_k a_{k'}(j_1 j_2 J)\rangle_{av(J)} A_k A_{k'} F^k F^{k'} \qquad (C\cdot 11)$$

$$+ \langle b_k b_{k'}(j_1 j_2 J)\rangle_{av(J)} B_k B_{k'} G^k G^{k'}$$

$$- 2\langle a_k b_{k'}(j_1 j_2 J)\rangle_{av(J)} A_k B_{k'} F^k G^{k'}] .$$

In this case, it is found that

$$\langle a_k a_{k'}(j_1 j_2 J)\rangle_{av(J)} = \langle b_k b_{k'}(j_1 j_2 J)\rangle_{av(J)} \qquad (C\cdot 12a)$$

$$= (2k+1)^{-1} \delta_{kk'} ,$$

$$\langle a_k b_{k'}(j_1 j_2 J)\rangle_{av(J)} = W(j_1 k k' j_2, j_1 j_2), \qquad (C\cdot 12b)$$

and consequently

$$\langle E^2(j_1 j_2 J) \rangle_{av(J)} = \sum_k (2k+1)^{-1} [A_k^2 (F^k)^2 + B_k^2 (G^k)^2] \qquad (C \cdot 13)$$

$$-2 \sum_k \sum_{k'} W(j_1 k k' j_2, j_1 j_2) A_k B_{k'} F^k G^{k'} .$$

For $k=0$, we have $a_k=1$, and Eqs. (C·12) reduce to the result (C·9). Knowing the first two moments of the distribution, we can then also calculate the variance $\Delta^2 E$. All terms involving F^0 drop out in the evaluation of $\Delta^2 E$.

Now suppose we have a transition of the form

$$(j_1 j_3)_J \rightarrow (j_2 j_3)_{J'} .$$

Due to configuration splitting in both initial and final state, the single particle line $j_1 \rightarrow j_2$ is split into various lines at different energies. Consider a given component, say, the one leading from state J to J'. Its energy is given by

$$E(j_1 j_3 J \rightarrow j_2 j_3 J') = E(j_1 j_3 J) - E(j_2 j_3 J'). \qquad (C \cdot 14)$$

Its strength, in units of that of the single particle line, can be shown to equal

$$S(J, J') = (2j_3+1)^{-1} (2J+1)(2J'+1) W^2(j_1 J j_2 J', j_3 \lambda). \qquad (C \cdot 15)$$

The quantity λ appearing in the Racah coefficient denotes the multipole order of the transition.

The average value of any quantity $Q(J, J')$ over both initial and final states is given by

$$\langle Q(J, J') \rangle_{av(J, J')} = \sum_J \sum_{J'} S(J, J') Q(J, J') / \sum_J \sum_{J'} S(J, J'). \qquad (C \cdot 16)$$

The sum in the denominator is unity.

In this way we can readily calculate the average energy of the line distribution and the average value of E^2. In evaluating these averages, it should be noted that the average of any quantity depending only on J (or only on J') is just the average defined in Eq. (C·8). Thus, since

$$\sum_{J'} (2J'+1) W^2(j_1 J j_2 J', j_3 \lambda) = (2j_1+1)^{-1} \qquad (C \cdot 17)$$

independent of the value of J or λ, we have

$$\langle Q(J) \rangle_{av(J, J')} = \sum (2J+1) Q(J) / \sum (2J+1) = \langle Q(J) \rangle_{av(J)}. \qquad (C \cdot 18)$$

If there is no interaction between the electrons in the final (or initial) state, then, as expected, all the moments of the line distribution are the same as those for the initial (or final) state. Another interpretation of this result is that for transition arrays between configurations of non-equivalent particles (i.e. in different orbits), the states are populated according to their statistical weight.

We also see from the above that the average energy of the lines is simply the difference between average energies of initial and final configurations.

$$\langle E(j_1 j_3 J \rightarrow j_2 j_3 J') \rangle_{av(J, J')} = \langle E(j_1 j_3 J) \rangle_{av(J)} \qquad (C \cdot 19)$$

$$- \langle E(j_2 j_3 J') \rangle_{av(J')}.$$

In order to calculate the average of E^2 for the line array, we also need the average of quantities depending on both J and J'. Thus

$$\langle E^2(j_1 j_3 J \rightarrow j_2 j_3 J') \rangle_{av(J, J')} = \langle E^2(j_1 j_3 J) \rangle_{av(J)} + \langle E^2(j_2 j_3 J') \rangle_{av(J')} \qquad (C \cdot 20)$$

$$- 2 \langle E(j_1 j_3 J') E(j_2 j_3 J') \rangle_{av(J, J')}.$$

In order to calculate the last term, we need averages such as

$$\langle a_{k_1}(j_1 j_3 J) a_{k_2}(j_2 j_3 J') \rangle_{av(J, J')}.$$

These can be calculated with the help of well-known sum rules involving Racah coefficients.[7] The results are

$$\langle a_{k_1}(j_1 j_3 J) a_{k_2}(j_2 j_3 J') \rangle_{av(J, J')} \qquad (C \cdot 21a)$$

$$= [(2j_1 + 1)(2j_2 + 1)]^{1/2} (2k + 1)^{-1} W(j_1 k_1 \lambda j_2, j_1 j_2) \delta_{k_1, k_2}$$

$$\langle a_{k_1}(j_1 j_3 J) b_{k_2}(j_2 j_3 J') \rangle_{av(J, J')} \qquad (C \cdot 21b)$$

$$= [2j_1 + 1)(2j + 1)]^{1/2} W(j_1 k_1 \lambda j_2, j_1 j_2) W(j_2 k_1 k_2 j_3, j_2 j_3)$$

$$\langle b_{k_1}(j_1 j_3 J) a_{k_2}(j_2 j_3 J') \rangle_{av(J, J')} \qquad (C \cdot 21c)$$

$$= [(2j_1 + 1)(2j_2 + 1)]^{1/2} W(j_2 k_2 \lambda j_1, j_2 j_1) W(j_1 k_2 k_1 j_3, j_1 j_3)$$

$$\langle b_{k_1}(j_1 j_3 J) b_{k_2}(j_2 j_3 J') \rangle_{av(J, J')} \qquad (C \cdot 21d)$$

$$= [(2j_1 + 1)(2j_2 + 1)]^{1/2} W^2(j_1 k_1 j_2 k_2, j_3 \lambda).$$

So far, we have only considered transitions between configurations of non-equivalent particles. Now suppose that we have a configuration of two equivalent particles, e.g. $(j_1)^2_J$. In this case, only even values of J are allowed by the exclusion principle. The energy for each of the allowed states is given in terms of direct Slater integrals F^k alone. Thus

$$E(j_1^2 J) = \sum_k a_k A_k F^k. \qquad (C \cdot 22)$$

The direct terms, a_k, A_k, F^k, are defined the same as for non-equivalent particles. In calculating averages, we must be careful to sum only over the allowed values of J. This can be accomplished by introducing a projection operator $P(J)$:

$$P(J) = 1/2[1 + (-1)^J] \qquad (C \cdot 23)$$

which equals 1 (or 0) for allowed (or forbidden) states. The average of any quantity is now given by

$$\langle Q(J) \rangle_{av(even\ J)} = \sum (2J + 1) P(J) Q(J) / \sum (2J + 1) P(J) \qquad (C \cdot 24)$$

where the sum can now go over *all* values of J (up to $2j$). This expression

can, in turn, be rewritten in terms of the previously defined average given in Eq. (C·8). Thus we find

$$\langle Q(J) \rangle_{av(even\ J)} = D(j) \{ \langle Q(J) \rangle_{av(J)} + \langle (-1)^J (Q(J) \rangle_{av(J)} \} \qquad (C·25a)$$

where

$$D(j_1) = [1 + \langle (-1)^J \rangle_{av(J)}]^{-1} . \qquad (C·25b)$$

The calculation of the average energy is quite simple. We have

$$\langle (-1)^J \rangle_{av(J)} = -(2j_1+1)^{-1} . \qquad (C·26)$$

Thus

$$D(j_1) = 1 + (2j_1)^{-1} . \qquad (C·27)$$

Also, for equivalent particles it is seen that

$$a_k = (-1)^{J-1} b_k . \qquad (C·28a)$$

Thus

$$\langle (-1)^J a_k \rangle_{av(J)} = -\langle b_k \rangle_{av(J)} . \qquad (C·28b)$$

Consequently, the average energy is given by

$$\langle E(j_1^2 J) \rangle_{av(even\ J)} = \sum_k \langle a_k(j_1 j_1 J) \rangle_{av(even\ J)} A_k F^k \qquad (C·29)$$

where

$$\langle a_k \rangle_{av(even\ J)} = D(j_1) \{ \langle a_k \rangle_{av(J)} - \langle b_k \rangle_{av(J)} \} \qquad (C·30)$$

$$= [\delta_{k0} - (2j_1+1)^{-1}] / [1 - (2j_1+1)^{-1}] .$$

Also,

$$\langle E^2(j_1^2 J) \rangle_{av(even\ J)} = \sum_k \sum_{k'} \langle a_k a_{k'} \rangle_{av(even\ J)} A_k A_{k'} F^k F^{k'} \qquad (C·31)$$

where

$$\langle a_k a_{k'} \rangle_{av(even\ J)} = D(j_1) \{ \langle a_k a_{k'} \rangle_{av(J)} - \langle a_k b_{k'} \rangle_{av(J)} \} \qquad (C·32)$$

$$= [(2k+1)^{-1} \delta_{kk'} - W(j_1 kk' j_1, j_1 j_1)] / [1 - (2j_1+1)^{-1}] .$$

Finally, consider the splitting of the line array:

$$(j_1^2)_J \rightarrow (j_1 j_2)_{J'} .$$

The relative line intensities of all allowed transitions (i.e. with even J) are the same as for non-equivalent particles, i.e. for the transition

$$(j_1 j_1)_J \rightarrow (j_1 j_2)_{J'} .$$

However, only even values of J are allowed. This must be taken into account in calculating the averages.

From the argument given above, we see that

$$\langle Q(J, J')\rangle_{av(J', even\ J)} = \sum_J \sum_{J'} S(J, J') P(J) Q(J, J') / \sum_J \sum_{J'} S(J, J') P(J) \quad (C\cdot33)$$

$$= D(j_1) \left[\langle Q(J, J')\rangle_{av(J, J')} + \langle (-1)^J Q(J, J')\rangle_{av(J, J')} \right].$$

The average energy of the line array is

$$\langle E(j_1^2 J \to j_1 j_2 J')\rangle_{av(J', even\ J)} \qquad\qquad\qquad (C\cdot34)$$

$$= \langle E(j_1^2 J)\rangle_{av(J', even\ J)} - \langle E(j_1 j_2 J')\rangle_{av(J', even\ J)}.$$

Now it follows from Eq. (C·18) that

$$\langle Q(J)\rangle_{av(even\ J, J')} = \langle Q(J)\rangle_{av(even\ J)}. \qquad\qquad (C\cdot35)$$

Thus, the first term of (C·34) is simply $\langle E(j_1^2 J)\rangle_{av(even\ J)}$. In order to calculate the average energy in the final state, we also need the expressions

$$\langle (-1)^J a_k(j_1 j_2 J')\rangle_{av(J, J')} \qquad\qquad\qquad (C\cdot36a)$$

$$= - \left[(2j_2+1)/(2j_1+1) \right]^{1/2} W(j_1 \lambda k j_2, j_2 j_1),$$

$$\langle (-1)^J b_k(j_1 j_2 J)\rangle_{av(J, J')} \qquad\qquad\qquad (C\cdot36b)$$

$$= - \left[(2j_2+1)/(2j_1+1) \right]^{1/2} (2\lambda+1)^{-1} \delta_{k\lambda}.$$

This average is different from the average $E(j_2 j_3 J')_{av(J')}$ calculated previously. The significance of this difference is that for transitions between configurations of equivalent particles, the states may not be populated purely according to their statistical weight.

To calculate the average of E^2 for the line array, we proceed in the same way as before. Thus

$$\langle E^2(j_1^2 J \to j_1 j_2 J')\rangle_{av(J', even\ J)} \qquad\qquad\qquad (C\cdot37)$$

$$= \langle E^2(j_1^2 J)\rangle_{av(J', even\ J)} + \langle E^2(j_1 j_2 J')\rangle_{av(J', even\ J)}$$

$$- 2\langle E(j_1^2 J) E(j_1 j_2 J')\rangle_{av(J', even\ J)}.$$

The first term is given by

$$\langle E^2(j_1^2 J)\rangle_{av(even\ J)}.$$

The last term can also be calculated in terms of quantities written above. The required averages are of the form

$$\langle a_k(j_1^2 J) \phi_{k'}(j_1 j_2 J')\rangle_{av(J', even\ J)} \qquad\qquad\qquad (C\cdot38)$$

$$= D(j_1) \left[\langle a_k \phi_{k'}\rangle_{av(J, J')} + \langle (-1)^J a_k \phi_{k'}\rangle_{av(J, J')} \right]$$

$$(\phi = a\ or\ b).$$

The average of $a_k \phi_{k'}$ has been given above. The other term equals

$$\langle (-1)^J a_k \phi_{k'}\rangle_{av(J, J')} = - \langle b_k \phi_{k'}\rangle_{av(J, J')}. \qquad\qquad (C\cdot39)$$

In order to calculate the second term in Eq. (C·37), we need some additional

expressions.

⸳It can be shown, using known relations given in reference 7) that

$$\langle (-1)^J a_k a_{k'} (j_1 j_2 J') \rangle_{av(J', \; even \; J)} = -(2j_2+1)(-1)^\gamma X \begin{pmatrix} k & j_1 & j_1 \\ j_2 & k' & j_2 \\ j_2 & j_1 & \lambda \end{pmatrix} \quad (C \cdot 40a)$$

where X denotes a $9j$ coefficient and γ is the sum of all its nine indices. Also

$$\langle (-1)^J b_k b_{k'} (j_1 j_2 J') \rangle_{av(J', \; even \; J)} = -(2j_2+1)(-1)^\gamma X \begin{pmatrix} k & j_1 & j_2 \\ j_2 & k' & j_1 \\ j_1 & j_2 & \lambda \end{pmatrix}, \quad (C \cdot 40b)$$

$$\langle (-1)^J a_k b_{k'} (j_1 j_2 J') \rangle_{av(J', \; even \; J)} \qquad\qquad\qquad (C \cdot 40c)$$
$$= -(2j_2+1) W(j_2 k j_1 k', j_2 \lambda) W(j_1 k j_2 k', j_1 \lambda).$$

All of the above results can be shown to hold with only minor modifications in *L-S* coupling. Thus, consider the configuration $(l_1 l_2)_L$. The energy of terms belonging to this configuration is given by

$$E(l_1 l_2 L) = \sum_k (a_k A_k F^k \pm b_k B_k G^k) \qquad (C \cdot 41)$$

where the $+$ or $-$ sign applies depending on whether the total spin S equals 0 or 1. In this expression, the quantities a_k, b_k, A_k, B_k, have the same form as in the *j-j* coupling case, if we replace each j by the appropriate l, e.g. j_1 by l_1. The reduced matrix element appearing in A_k and B_k is given by a slightly different expression than before:

$$\langle l_1 \| c^k \| l_2 \rangle = (2l_1+1)^{1/2} (l_1 0 k 0 | l_2 0). \qquad (C \cdot 42)$$

(The Clebsch-Gordan coefficient vanishes automatically when $l_1 + l_2 + k$ is odd.)

Since states of spin 1 have a statistical weight three times as large as those of spin 0 (but the same L), the average energy averaged over spins (for given L) is

$$\langle E \rangle_{av(S)} = \sum_k (a_k A_k F^k - (1/2) b_k B_k G^k). \qquad (C \cdot 43)$$

The averages of a_k, b_k (and their products) over L values are given by the same kind of expressions as before. However, as in Eq. (C·43), we obtain an extra factor of $1/2$ in all terms containing a *single* exchange term G^k. Furthermore, when we deal with equivalent particles, the appropriate projection factor is

$$P(L, \; S) = (1/2) [1 + (-1)^{L+S}], \qquad (C \cdot 44)$$

i.e. for the $(l^2)_L$ configuration, states with even (odd) L must have $S=0(1)$. Averaging over spins, we find that

$$\langle (-1)^{L+S} \rangle_{av(S)} = -(1/2)(-1)^L \qquad (C \cdot 45)$$

and thus

$$\langle Q(L, S)\rangle_{av(S, \text{ allowed } L)} \tag{C·46}$$

$$= [\langle Q(L, S)\rangle_{av(L, S)} - (1/2)\langle(-1)^L Q(L, S)\rangle_{av(L, S)}]/[1 - (1/2)\langle(-1)^L\rangle_{av(L)}].$$

However, the signs of all averages of the form $\langle(-1)^L\phi(L')\rangle_{av(L, L')}$ which appear in the expressions for $Q(L, L', S)_{av(S, L', \text{allowed } L)}$, are now reversed from those for *j-j* coupling. Thus, for example,

$$\langle(-1)^L\rangle_{av(L)} = (2l+1)^{-1}, \tag{C·47a}$$

$$\langle(-1)^L a_k(l_1 l_2 L')\rangle_{av(L, L')} = [(2l_2+1)/(2l_1+1)]^{1/2} W(l, \lambda k l_2, l_2 l_1). \tag{C·47b}$$

As an application of the above results, consider the transition array

$$\left(p\frac{3}{2}\right)^2 \rightarrow \left(p\frac{3}{2} s\frac{1}{2}\right).$$

There are only two states each for the initial and final configuration. For $(3/2)^2$, the initial configuration denoted by i, we have a state with $J=0$ at energy $F^0 + (5/25)F^2$, and a state with $J=2$ at an energy $F^0 - (3/25)F^2$. For the final (f) configuration $(3/2\ 1/2)$ we have the states $J=1$ at $F^0 + (1/9)G^1$ and $J=2$ at $F^0 - (3/9)G^1$.

The relative intensity of the transition lines can be calculated using Eq. (C·15) above. We suppose it is a dipole transition $(\lambda=1)$. Assume for simplicity that the Slater integral F^0 is the same in the initial and final state; thus it does not contribute to the energy of any line. The relative intensity and energy of the lines is given in Table III.

Table III.
Relative intensity and energy of lines in the $(p(3/2))^2 \rightarrow (p(3/2)s(1/2))$ transition array.
(The Slater integral F^0 is assumed not to contribute to the line energy.)

J_i	J_f	Rel. Intensity	Energy
0	1	2/12	$(5/25)F^2 - (1/9)G^1$
0	2	0	$(5/25)F^2 + (3/9)G^1$
2	1	5/12	$-(3/25)F^2 - (1/9)G^1$
2	2	5/12	$-(3/25)F^2 + (3/9)G^1$

The average energy can be calculated explicitly and we find

$$\langle E\rangle_{av(i, f)} = -\frac{1}{15}F^2 + \frac{2}{27}G^1. \tag{C·48}$$

Also

$$\langle E^2\rangle_{av(i, f)} = \frac{7}{375}(F^2)^2 + \frac{13}{243}(G^1)^2 - \frac{4}{135}F^2 G^1 \tag{C·49}$$

and thus

$$\langle \Delta^2 E \rangle = \frac{16}{1125}(F^2)^2 + \frac{35}{729}(G^1)^2 - \frac{8}{405}F^2 G^1 . \tag{C·50}$$

These averages can also be calculated by using our general formulas. Thus

$$\langle E(i) \rangle_{av(i, f)} = \langle a_2 \rangle_{av(J', \text{ even } J)} A_2 F^2 \tag{C·51}$$

where

$$a_2 = a_2 \left(\begin{array}{cc} \frac{3}{2} & \frac{3}{2} \\ & & J \end{array} \right) .$$

Now

$$\langle a_2 \rangle_{av(J', \text{even } J)} = D_J [\langle a_2 \rangle_{av(J)} - \langle b_2 \rangle_{av(J)}] = \frac{4}{3}\left(0 - \frac{1}{4}\right) = -\frac{1}{3} \tag{C·52}$$

and

$$A_2 = \frac{1}{5} .$$

Consequently

$$\langle E(i) \rangle_{av(i, f)} = -\frac{1}{15}F^2 , \tag{C·53}$$

while the other term

$$\langle E(f) \rangle_{av(i, f)} = +\langle b_1 \rangle_{av(J', \text{ even } J)} B_1 G_1 \tag{C·54}$$

where

$$\langle b_1 \rangle_{av(\text{even } J, J')} = D_J [\langle b_1 \rangle_{av(J, J')} + \langle (-1)^J b_1 \rangle_{av(J, J')}] \tag{C·55}$$

$$= \frac{4}{3}[8^{-1/2} - 18^{-1/2}] = \frac{\sqrt{2}}{9}$$

and

$$B_1 = \frac{\sqrt{2}}{3} .$$

Thus

$$\langle E(f) \rangle_{av(i, f)} = -\frac{2}{27}G^1 \tag{C·56}$$

which agrees with our explicitly calculated average.

The results in Eqs. (C·53) and (C·56) agree with our earlier expression in Eq. (C·48).

The evaluation of $\langle E^2 \rangle_{av}$ proceeds similarly:
We have

$$\langle E^2(i \to f)\rangle_{av(i, f)} = \langle E^2(i)\rangle_{av(i, f)} + \langle E^2(f)\rangle_{av(i, f)} - 2\langle E(i)E(f)\rangle_{av(i, f)} . \quad (C\cdot57)$$

Now

$$\langle E^2(i)\rangle_{av(i, f)} = \langle a_2{}^2\rangle_{av(J', \text{ even } J)} A_2{}^2(F^2)^2 \quad (C\cdot58)$$

and also

$$\langle E^2(f)\rangle_{av(i, f)} = \langle b_1{}^2\rangle_{av(J', \text{ even } J)} B_1{}^2(G^1)^2, \quad (C\cdot59)$$

$$\langle E(i)E(f)\rangle_{av(i, f)} = \langle a_2 b_1\rangle_{av(J', \text{ even } J)} A_2 B_1 F^2 G^1 . \quad (C\cdot60)$$

The averages are given as follows:

$$\langle a_2{}^2\rangle_{av(J', \text{ even } J)} = D_J[\langle a_2{}^2\rangle_{av(J, J')} - \langle a_2 b_2\rangle_{av(J, J')}] \quad (C\cdot61)$$

$$= \left(\frac{4}{3}\right)\left(\frac{1}{5} + \frac{3}{20}\right) = \frac{7}{15},$$

$$\langle b_1{}^2\rangle_{av(J', \text{ even } J)} = D_J[\langle b_1{}^2\rangle_{av(J, J')} + \langle(-1)^J{}_{av(J, J')} b_1{}^2\rangle] \quad (C\cdot62)$$

$$= \frac{4}{3}\left(\frac{1}{3} - \frac{11}{72}\right) = \frac{13}{54},$$

$$\langle a_2 b_1\rangle_{av(J', \text{ even } J)} = D_J[\langle a_2 b_1\rangle_{av(J, J')} - \langle b_2 b_1\rangle_{av(J, J')}] \quad (C\cdot63)$$

$$= \frac{4}{3}\,(0 - 1\sqrt{72}) = -\frac{\sqrt{2}}{9} .$$

Substituting these numbers into Eq. (C·57), we obtain the earlier result given in Eq. (C·49).

References

1) Such relations between mean interactions energies are, in fact, well known.

2) Strengths of individual lines and sum rules involving line strengths but not energies, have previously been studied in the literature. See, for example, D. H. Menzel and L. Goldberg, Ap. J. **84** (1936), 1; F. Rohrlich, Ap. J. **129** (1959), 441–449. For comprehensive discussions of line strengths see Condon and Shortley, *Theory of Atomic Spectra*, and W. Slater, *Quantum Theory of Atomic Structure*, (McGraw-Hill Company, New York, 1960) Vol. II, Chap. 25. The latter contains an extensive bibliography.

3) See G. Racah, Phys. Rev. **63** (1943), 347, for a simple discussion of the method of fractional parentage coefficients and its applications.

4) For a more detailed discussion of this model and some general considerations regarding term and line array distributions, see S. A. Moszkowski, *Some Statistical Properties of Level and Line Distributions in Atomic Spectra*, The RAND Corporation, Research Memorandum RM-2610-AEC, November 8, 1960.

5) The dominant central-field term in the multipole expansion (Slater integral F°) does not lead to any splitting of terms, and consequently it does not affect the shape of our distribution.

6) G. Racah, Phys. Rev. **62** (1942), 438.

7) Properties of the Racah coefficients and other quantities used in this Appendix are summarized by H. Horie and T. Ishidzu, ed., in Part I of *Tables of the Racah Coefficients*, (Pan Pacific Press, Tokyo, 1960). See also, A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton University Press, Princeton, 1957); M. E. Rose, *Elementary Theory of Angular Momentum* (Wiley, New York, 1957); and Rotenberg, Bivins, Metropolis and Wooten, *The 3-j and 6-j Symbols* (Cambridge University Press, MIT, 1959).