Proof of Moszkowski's Formula for the Variance of Term Energies in an Electronic Configuration of the Form l^n*

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The formula in question is

$$\sigma^2(E \text{ in } l^n) = [n(n-1)(4l+2-n)(4l+2-n-1)/2(4l)(4l-1)]\sigma^2(E \text{ in } l^2).$$

The proof makes use of probability matrices rather than of fractional parentage coefficients.

I. INTRODUCTION

THE mean interaction energy in an electronic configuration l^n is known to be related to the mean interaction energy in the configuration l^2 by the simple rule

$$\mu(E \text{ in } l^n) = \binom{n}{2} \mu(E \text{ in } l^2), \tag{1.1}$$

where it is understood that the two-electron interactions have the same strength in the configurations l^n and l^2. Moszkowski[1] has suggested the following formula relating the mean-square deviation of the interaction energy from its mean value in l^n with the corresponding quantity in l^2:

$$\sigma^2(E \text{ in } l^n) = \frac{\binom{n}{2}\binom{N_0-n}{2}}{\binom{N_0-2}{2}} \sigma^2(E \text{ in } l^2), \tag{1.2}$$

where $N_0 = 4l+2$, the number of electrons in a complete l subshell. Moszkowski verified Eq. (1.2) in a few particular cases and gave an ingenious plausibility argument for it, based on the method of second quantization.

It is natural to attempt a proof by expressing σ^2 (E in l^n) in terms of two-electron matrix elements, by means of the now-standard techniques introduced by Racah.[2] However, because one has to deal with the squares of interaction matrix elements (or the matrix elements of squares of interaction operators), this approach quickly leads to rather forbidding complications. An alternative and, as it turns out, much simpler approach, followed here, employs probability matrices of a kind introduced by Bacher and Goudsmit[3] in 1934.

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[1] S. A. Moszkowski, Progr. Theoret. Phys. (Kyoto) **28**, 1 (1962).

[2] G. Racah, Phys. Rev. **62**, 438 (1942); **63**, 367 (1943); referred to in subsequent footnotes by the roman numerals II, III.

[3] R. F. Bacher and S. Goudsmit, Phys. Rev. **46**, 948 (1934).

II. PROBABILITY MATRICES

Let $P(l^m\Gamma_1 l^{n-m}\Gamma_2 | l^n\Gamma)$ denote the probability that, when an n-electron system is in the state $l^n\Gamma$, a given m-electron subsystem of it will be found in the state $l^m\Gamma_1$ and the complementary $(n-m)$-electron subsystem will be found in the state $l^{n-m}\Gamma_2$. Clearly,

$$\begin{aligned} P(l^m\Gamma_1 l^{n-m}\Gamma_2 | l^n\Gamma) &= P(l^{n-m}\Gamma_2 l^m\Gamma_1 | l^n\Gamma) \\ &= |\langle l^m\Gamma_1 l^{n-m}\Gamma_2] l^n\Gamma\rangle|^2, \end{aligned} \tag{2.1}$$

the square of a cfp (coefficient of fractional parentage). The quantity

$$P(l^m\Gamma_1 | l^n\Gamma) \equiv \sum_{\Gamma_2} P(l^m\Gamma_1 l^{n-m}\Gamma_2 | l^n\Gamma) \tag{2.2}$$

is the probability that a given m-electron subsystem will be found in the state $l^m\Gamma_1$ when its parent n-electron system is known to be in the state Γ. The quasiunitarity of the cfp matrices ensures that

$$\sum_{\Gamma_1\Gamma_2} P(l^m\Gamma_1 l^{n-m}\Gamma_2 | l^n\Gamma) = \sum_{\Gamma_1} P(l^m\Gamma_1 | l^n\Gamma) = 1. \tag{2.3}$$

The probabilities $P(l^m\Gamma_1 | l^n\Gamma)$ contain less information than the corresponding cfp's—much less if $n-m \geq 2$—but have simpler properties, of which the three following are especially useful.

(*i*) *Composition law.* By elementary probability theory,

$$\sum_{\Gamma_2} P(l^m\Gamma_1 | l^r\Gamma_2) P(l^r\Gamma_2 | l^n\Gamma) = P(l^m\Gamma_1 | l^n\Gamma) \qquad (m<r<n), \tag{2.4}$$

where the sum runs over all states Γ_2 of l^n (in the sequel all such sums will be understood to be complete). Starting with the probabilities $P(l^{n-1}\Gamma_1 | l^n\Gamma)$, one can generate all the probability matrices $\|P(l^m\Gamma_1 | l^n\Gamma)\|$ by successive applications of Eq. (2.4) with $r=m+1$.

(*ii*) *Completeness.* Let $\tilde{\omega}(\Gamma)[=(2S+1)(2L+1)]$ denote the statistical weight (degeneracy) of a state $l^n\Gamma$. The total number of nondegenerate states of l^n is $\binom{N_0}{n}$. Hence, the probability of realizing the degenerate state $l^n\Gamma$ is

$$P(l^n\Gamma)=\tilde{\omega}(\Gamma)\Big/\binom{N_0}{n}. \tag{2.5}$$

Now, by elementary probability theory, the joint probability $P(ab)$ of two states a, b is given by

$$P(ab)=P(a|b)P(b); \tag{2.6}$$

and

$$P(a)=\sum_b P(ab)\,,\quad P(b)=\sum_a P(ab)\,. \tag{2.7}$$

Hence,

$$\sum_\Gamma P(l^m\Gamma_1|l^n\Gamma)P(l^n\Gamma)=\sum_\Gamma P(l^m\Gamma_1 l^n\Gamma)=P(l^m\Gamma_1)\,. \tag{2.8}$$

(*iii*) *Relation between probabilities in complementary configurations.* To every state $l^n\Gamma$ there corresponds a unique state of the complementary configuration l^{N_0-n}, which we may indicate by the same label Γ.[4] The decomposition

$$|l^n\Gamma\rangle=\sum_{\Gamma_1\Gamma_2}|l^m\Gamma_1\rangle|l^{n-m}\Gamma_2\rangle\langle l^2\Gamma_1 l^{n-m}\Gamma_2]\!]l^n\Gamma\rangle \tag{2.9}$$

corresponds to the decomposition

$$|l^{N_0-m}\Gamma_1\rangle=\sum_{\Gamma\Gamma_2}|l^{N_0-n}\Gamma\rangle|l^{n-m}\Gamma_2\rangle \times\langle l^{N_0-n}\Gamma l^{n-m}\Gamma_2]\!]l^{N_0-m}\Gamma_1\rangle. \tag{2.9$'$}$$

Racah[5] has given a relation between the cfp's that occur in the last two equations for the case $m=1$, from which a relation valid for any value of m can easily be derived. The same relation (apart from a phase factor) can be derived from elementary probability considerations, as follows. Let $P(abc)$ signify the joint probability of the three states, a, b, c. Clearly,

$$P(l^m\Gamma_1 l^{n-m}\Gamma_2 l^n\Gamma)=P(l^{N_0-n}\Gamma l^{n-m}\Gamma_2 l^{N_0-m}\Gamma_1)\,. \tag{2.10}$$

It follows from (2.6) that

$$\begin{aligned}P(l^m\Gamma_1 l^{n-m}\Gamma_2|l^n\Gamma)P(l^n\Gamma)&\\ =P(l^{N_0-n}\Gamma l^{n-m}\Gamma_2|l^{N_0-m}\Gamma_1)P(l^{N_0-m}\Gamma_1)&\qquad(2.11)\\ =P(l^{N_0-n}\Gamma l^{n-m}\Gamma_2|l^{N_0-m}\Gamma_1)P(l^m\Gamma_1)\,,&\end{aligned}$$

which is the desired relation.

III. PROOF OF MOSZKOWSKI'S FORMULA

Let G_n denote a symmetric sum of two-electron interactions g_{ij} among n electrons:

$$G_n=\sum_{\text{all pairs}} g_{ij}\,. \tag{3.1}$$

If G_m is diagonal in the Γ scheme, it follows from (2.9) and (2.1) that

$$\begin{aligned}\langle l^n\Gamma|G_n|l^n\Gamma\rangle&=\frac{\binom{n}{2}}{\binom{m}{2}}\langle l^n\Gamma|G_m|l^n\Gamma\rangle\\ &=\frac{\binom{n}{2}}{\binom{m}{2}}\sum_{\Gamma_1\Gamma_2}\langle l^m\Gamma_1|G_m|l^m\Gamma_1\rangle P(l^m\Gamma_1 l^{n-m}\Gamma_2|l^n\Gamma) &(3.2)\\ &=\frac{\binom{n}{2}}{\binom{m}{2}}\sum_{\Gamma_1}\langle l^m\Gamma_1|G_m|l^m\Gamma_1\rangle P(l^m\Gamma_1|l^n\Gamma)\,. &(3.2\text{b})\end{aligned}$$

Multiplying Eq. (3.2b) by $P(l^n\Gamma)$ and summing over Γ, we obtain, with the help of the completeness relation (2.8),

$$\begin{aligned}\mu(G_n)&\equiv\sum_\Gamma\langle l^n\Gamma|G_n|l^n\Gamma\rangle P(l^n\Gamma)\\ &=\frac{\binom{n}{2}}{\binom{m}{2}}\sum_{\Gamma_1}\langle l^m\Gamma_1|G_m|l^m\Gamma_1\rangle P(l^m\Gamma_1)\\ &\equiv\frac{\binom{n}{2}}{\binom{m}{2}}\mu(G_m)\,, &(3.3)\end{aligned}$$

which contains Eq. (1.1) as a special case. The "fluctuating part" of G_n is defined as

$$\tilde{G}_n\equiv G_n-\mu(G_n)\,. \tag{3.4}$$

[4] See Ref. 2, paper II.
[5] See Ref. 2, paper III.

Subtracting (3.3) from (3.2), we obtain

$$\langle l^n\Gamma|\tilde{G}_n|l^n\Gamma\rangle = \frac{\binom{n}{2}}{\binom{m}{2}} \sum_{\Gamma_1\Gamma_2} \langle l^m\Gamma_1|\tilde{G}_m|l^m\Gamma_1\rangle P(l^m\Gamma_1 l^{n-m}\Gamma_2|l^n\Gamma). \quad (3.5)$$

We consider two special cases of the last equation: $n=n$, $m=2$; and $n=N_0-2$, $m=N_0-n$. Thus, we require both G_n and G_2 to be diagonal in the Γ scheme. In the first case,

$$\langle l^n\Gamma|\tilde{G}_n|l^n\Gamma\rangle = \binom{n}{2} \sum_{\Gamma_1'\Gamma_2'} \langle l^2\Gamma_1'|\tilde{G}_2|l^2\Gamma_1'\rangle \times P(l^2\Gamma_1' l^{n-2}\Gamma_2'|l^n\Gamma); \quad (3.6)$$

in the second,

$$\langle l^{N_0-2}\Gamma_1|\tilde{G}_{N_0-2}|l^{N_0-2}\Gamma_1\rangle = \frac{\binom{N_0-2}{2}}{\binom{N_0-n}{2}} \sum_{\Gamma'\Gamma_2} \langle l^{N_0-n}\Gamma'|\tilde{G}_{N_0-n}|l^{N_0-n}\Gamma'\rangle \times P(l^{N_0-n}\Gamma' l^{n-2}\Gamma_2|l^{N_0-2}\Gamma_1). \quad (3.7)$$

We now assume that, for any value of m,

$$\langle l^m\Gamma|\tilde{G}_m|l^m\Gamma\rangle = \pm\langle l^{N_0-m}\Gamma|\tilde{G}_{N_0-m}|l^{N_0-m}\Gamma\rangle, \quad (3.8)$$

where the sign depends only on the nature of the interaction and not on the value of m. This relation is valid for a wide variety of interactions, including the Coulomb interaction and the spin-orbit interaction (taken separately). With the help of (3.8) and (2.11) we may write Eq. (3.7) in the form

$$\langle l^2\Gamma_1|\tilde{G}_2|l^2\Gamma_1\rangle P(l^2\Gamma_1) = \frac{\binom{N_0-2}{2}}{\binom{N_0-n}{2}} \sum_{\Gamma'\Gamma_2'} \langle l^n\Gamma'|\tilde{G}_n|l^n\Gamma'\rangle P(l^n\Gamma') \times P(l^2\Gamma_1 l^{n-2}\Gamma_2'|l^n\Gamma'). \quad (3.9)$$

This relation expresses the two-electron matrix elements as linear combinations of the n-electron elements, while Eq. (3.6) does just the reverse.

Multiplying (3.6) by the transpose of Eq. (3.9), we obtain

$$\sum_{\Gamma'\Gamma_2'} \langle l^n\Gamma|\tilde{G}_n|l^n\Gamma\rangle\langle l^n\Gamma'|\tilde{G}_n|l^n\Gamma'\rangle P(l^n\Gamma') \times P(l^2\Gamma_1 l^{n-2}\Gamma_2'|l^n\Gamma') = \frac{\binom{n}{2}\binom{N_0-n}{2}}{\binom{N_0-2}{2}} \sum_{\Gamma_1'\Gamma_2'} \langle l^2\Gamma_1|\tilde{G}_2|l^2\Gamma_1\rangle\langle l^2\Gamma_1'|\tilde{G}_2|l^2\Gamma_1'\rangle \times P(l^2\Gamma_1)P(l^2\Gamma_1' l^{n-2}\Gamma_2'|l^n\Gamma). \quad (3.10)$$

We now seek to invert the probability matrix $\|P(l^2\Gamma_1 l^{n-2}\Gamma_2|l^n\Gamma)\|$. In order to do this, we must first make it into a square matrix by adjoining the columns corresponding to nonantisymmetric states Γ. This can always be done, since the cfp matrix $\|\langle l^2\Gamma_1 l^{n-2}\Gamma_2|l^n\Gamma\rangle\|$ can always be eked out with extra columns to make it a true unitary matrix. Moreover, one can always ensure that the augmented probability matrix is nonsingular if the columns that correspond to antisymmetric states Γ are linearly independent. If this were not so, however, one could construct a linear combination of matrix elements $\langle l^n\Gamma|G_n|l^n\Gamma\rangle$ that would vanish identically for every interaction g_{12} that is diagonal in the Γ scheme —which is impossible.

Let $Q(l^2\Gamma_1 l^{n-2}\Gamma_2|l^n\Gamma)$ denote an element of the inverse of the matrix $\|P(l^2\Gamma_1 l^{n-2}\Gamma_2|l^n\Gamma)\|$. Then,

$$\sum_{\Gamma} P(l^2\Gamma_1 l^{n-2}\Gamma_2|l^n\Gamma)Q(l^2\Gamma_1' l^{n-2}\Gamma_2'|l^n\Gamma) = \delta_{\Gamma_1\Gamma_1'}\delta_{\Gamma_2\Gamma_2'}, \quad (3.11\text{a})$$

$$\sum_{\Gamma_1} P(l^2\Gamma_1 l^{n-2}\Gamma_2|l^n\Gamma)Q(l^2\Gamma_1 l^{n-2}\Gamma_2'|l^n\Gamma') = \delta_{\Gamma_2\Gamma_2'}\delta_{\Gamma\Gamma'}, \quad (3.11\text{b})$$

$$\sum_{\Gamma_2} P(l^2\Gamma_1 l^{n-2}\Gamma_2|l^n\Gamma)Q(l^2\Gamma_1' l^{n-2}\Gamma_2|l^n\Gamma') = \delta_{\Gamma_1\Gamma_1'}\delta_{\Gamma\Gamma'}. \quad (3.11\text{c})$$

Multiplying Eq. (3.10) by $Q(l^2\Gamma_1 l^{n-2}\Gamma_2|l^n\Gamma)$ and summing over Γ_1, Γ_2, Γ, we obtain, with the help of (3.11),

$$\sum_{\Gamma} |\langle l^n\Gamma|\tilde{G}_n|l^n\Gamma\rangle|^2 P(l^n\Gamma) = \frac{\binom{n}{2}\binom{N_0-n}{2}}{\binom{N_0-2}{2}} \sum_{\Gamma_1} |\langle l^2\Gamma_1|\tilde{G}_2|l^2\Gamma_1\rangle|^2 P(l^2\Gamma_1) \quad (3.12)$$

or

$$\sigma^2(G_n) = \frac{\binom{n}{2}\binom{N_0-n}{2}}{\binom{N_0-2}{2}} \sigma^2(G_2), \quad (3.13)$$

which is Moszkowski's formula.