Fermilab Library
0 1160 0026145 7

LYCEN 9344
Sept. 1993

LYCEN-9344

Coulomb energy averaged over the $n\ell^N$-atomic states with a definite spin

DEC 14 1993

M Kibler[1] and Yu F Smirnov[2] †

[1]Institut de Physique Nucléaire de Lyon, IN2P3-CNRS et Université Claude Bernard, 43 Boulevard du 11 Novembre 1918, F-69622 Villeurbanne Cedex, France

[2]Instituto de Física, Universidad Nacional Autonoma de Mexicó, Mexicó D F, Mexicó

Abstract. A purely group-theoretical approach, based upon the use of properties of fractional-parentage coefficients and isoscalar factors, is developed for the derivation of the Coulomb energy averaged over the states, with a definite spin, arising from an atomic configuration $n\ell^N$.

Submitted for publication in Journal of Physics B: Atomic, Molecular and Optical Physics

† Permanent address: Institute of Nuclear Physics, Moscow State University, 119899 Moscow, Russia.

1. Introduction

In the framework of an alternative parametrisation for the theory of complex spectra (Kibler 1975, Kibler and Katriel 1990, Kibler and Partensky 1991), Kibler and Katriel (1990) have conjectured a formula, viz,

$$^{2S+1}E_{\mathrm{av}}[nl^N] = \frac{1}{2}N(N-1)\Sigma + \frac{1}{2}\left[\frac{N}{2}(\frac{N}{2}+1) - S(S+1)\right]\Delta \tag{1}$$

giving the average Coulomb energy $E_{\mathrm{av}}[n\ell^N]$ for the states, with a fixed value of the spin S, which arise from an atomic configuration $n\ell^N$ of N equivalent electrons in a shell $n\ell$. In equation (1), the parameters Σ and Δ are defined through

$$^1E_{\mathrm{av}}[nl^2] = \Sigma + \Delta \qquad ^3E_{\mathrm{av}}[nl^2] = \Sigma \tag{2}$$

corresponding to the singlet ($S \equiv S_0 = 0$) and triplet ($S \equiv S_0 = 1$) states for the case $N = 2$. A formula equivalent to (1) and (2) has been derived independently (Karwowski and Bancewicz 1987). The approach used by Karwowski and Bancewicz (1987) (see also Diercksen and Karwowski 1987 and Karwowski, Valdemoro and Lain 1989) to obtain their formula is based on the method of moments.

It is the aim of this short paper to give a straightforward proof of (1) by making use of fractional-parentage coefficients and of an unusual sum rule satisfied by isoscalar factors for a chain of compact groups. Indeed, we work out (in § 2) an extension of formula (1), valid in the general case of a spin-independent two-body interaction, and then specialise it to the case of the Coulomb interaction. The relevant material (Racah's lemma and orthogonality-completeness property for Clebsch-Gordan coefficients or isoscalar factors) concerned with the group-theoretical approach of § 2 is relegated in the appendix (§3).

2. Average energies

In the Russell-Saunders coupling (or LS-coupling), the state vectors of the electronic configuration $n\ell^N$ (for atoms and ions) may be written as

$$\Psi \equiv |n\ell^N[f]\alpha LSM_LM_S). \tag{3}$$

Most of the symbols in (3) have their usual meaning. Let us simply precise that $[f]$ stands for a Young pattern, with two columns (say of lengths φ_1 and φ_2 with $\varphi_1 \geq \varphi_2$), which characterises the orbital part of Ψ. The spin part of Ψ may be described by the Young pattern $[\varphi] \equiv [\varphi_1\varphi_2]$, with two rows of lengths φ_1 and φ_2, which turns out to be the transposed pattern $[\tilde{f}]$ of $[f]$. The pattern $[\varphi]$ is (unambiguously) connected with the number of electrons N and the total spin S via

$$\varphi_1 + \varphi_2 = N \qquad \varphi_1 - \varphi_2 = 2S. \tag{4}$$

Finally, the symbol α in (3) collectively denotes the remaining labels that are necessary for a single-valued enumeration of the (allowed) atomic state vectors of the configuration $n\ell^N$.

The vectors Ψ are expressed in a basis adapted to the following chain of groups

$$U_{4\ell+2} \supset U_{2\ell+1}(\rightarrow SO_3 \rightarrow SO_2) \otimes U_2(\rightarrow SU_2 \rightarrow U_1). \tag{5}$$

Each of the vectors (3) spans the *antisymmetric* irreducible representation class (IRC) $\{1^N\}$ of the unitary group $U_{4\ell+2}$. The Young patterns $[f]$ and $[\varphi]$ characterise IRC's of the groups $U_{2\ell+1}$ and U_2 for the orbital and spin parts of Ψ, respectively. The quantum numbers L and S refer to IRC's of the subgroups SO_3 and SU_2 of $U_{2\ell+1}$ and U_2, respectively. Finally, the projections M_L and M_S indicate in turn IRC's of the subgroups SO_2 and U_1 of SO_3 and SU_2, respectively.

For a given configuration $n\ell^N$, the total number of the vectors (3) allowed by the Pauli principle coincides with the dimension of the IRC $\{1^N\}$ of the group $U_{4\ell+2}$. It is thus given by $\dim\{1^N\} = C^N_{4\ell+2}$ in terms of binomial coefficients. Among these $C^N_{4\ell+2}$ state vectors, we select the ones having a fixed value S of the spin. Obviously, the number of vectors Ψ with S fixed is nothing but the product $N_f(2S+1)$, where N_f is the dimension of the IRC $[f]$ of $U_{2\ell+1}$ and $2S+1$ may be visualised as the dimension N_φ of the IRC $[\varphi]$ of U_2.

In the present paper, we are interested in the average energy

$$^{2S+1}E_{\rm av}[n\ell^N] = \frac{1}{N_f}\,\frac{1}{2S+1}\sum_{\alpha L}\sum_{M_L}\sum_{M_S}(n\ell^N[f]\alpha LSM_LM_S|V|n\ell^N[f]\alpha LSM_LM_S) \tag{6}$$

where V is a spin-independent two-body Hamiltonian

$$V = \sum_{j>i=1}^{N} V_{ij} \quad \text{with} \quad V_{ij} \equiv V_{ij}(r_{ij}). \tag{7}$$

Equation (6) gives the average of V over the $N_f(2S+1)$ state vectors (3) having a fixed spin S. In equation (7), the sum on i and j is to be extended over the $N(N-1)/2$ two-electron interactions V_{ij} ; furthermore, V_{ij} depends only on the distance r_{ij} between the electrons i and j.

Invariance of V under the rotation group SO_3 and the spin group SU_2 ensures that (6) can be rewritten as

$$^{2S+1}E_{\rm av}[n\ell^N] = \frac{1}{N_f}\sum_{\alpha L}(2L+1)\,(n\ell^N\alpha LS|V|n\ell^N\alpha LS). \tag{8}$$

The next step is to introduce coefficients of fractional parentage in order to calculate

the matrix elements of V in (8). This leads to (Racah 1943)

$$
\begin{aligned}
(n\ell^N\alpha LS|V|n\ell^N\alpha LS) \;=\; \frac{1}{2}\,N(N-1) \sum_{\alpha' L' S'} \sum_{L_0 S_0} & \\
& (\ell^N\alpha LS\{|\ell^{N-2}\alpha' L' S', \ell^2 L_0 S_0) \\
& (n\ell^2 L_0 S_0|V_{12}|n\ell^2 L_0 S_0) \\
& (\ell^{N-2}\alpha' L' S', \ell^2 L_0 S_0|\}\ell^N\alpha LS).
\end{aligned}
\tag{9}
$$

Following Racah (1949, 1951) and Neudatchin and Smirnov (1968), the two-particle coefficient of fractional parentage $(\ell^N\,\{|\ell^{N-2},\ell^2) = (\ell^{N-2},\ell^2|\}\,\ell^N)^*$ in (9) can be developed as

$$
\begin{aligned}
(\ell^N\alpha LS\{|\ell^{N-2}\alpha' L' S', \ell^2 L_0 S_0) \;=\; & \sqrt{\frac{n_{f'} n_{f_0}}{n_f}} \\
& (\ell^N[f]\alpha L\{|\ell^{N-2}[f']\alpha' L', \ell^2[f_0]L_0) \\
& (s^N[\tilde{f}]S\{|s^{N-2}[\tilde{f}']S', s^2[\tilde{f}_0]S_0)
\end{aligned}
\tag{10}
$$

where $s = 1/2$. In equation (10), the IRC's $[f]$, $[f']$ and $[f_0]$ refer to the group $U_{2\ell+1}$. However, the symbols n_f, $n_{f'}$ and n_{f_0} denote the dimensions of $[f]$, $[f']$ and $[f_0]$ as considered as IRC's of the permutation groups S_N, S_{N-2} and S_2, respectively. From a group-theoretical viewpoint, the fractional-parentage coefficient $(\ell^N\alpha LS\{|\ell^{N-2}\alpha' L' S', \ell^2 L_0 S_0)$ is identical to the isoscalar factor $(\{1^{N-2}\}\alpha' L' S' + \{1^2\}L_0 S_0|\{1^N\}\alpha LS)$ for the chain $U_{4\ell+2} \supset SO_3 \otimes SU_2$ (Racah 1951). Equation (10) then corresponds to the factorization (see Racah 1949, 1951)

$$
\begin{aligned}
(\{1^{N-2}\}\alpha' L' S' + \{1^2\}L_0 S_0|\{1^N\}\alpha LS) \;=\; & (\{1^{N-2}\}[f'][\tilde{f}'] + \{1^2\}[f_0][\tilde{f}_0]|\{1^N\}[f][\tilde{f}]) \\
& ([f']\alpha' L' + [f_0]L_0|[f]\alpha L) \\
& ([\tilde{f}']S' + [\tilde{f}_0]S_0|[\tilde{f}]S)
\end{aligned}
\tag{11}
$$

in terms of isoscalar factors for the chains $U_{4\ell+2} \supset U_{2\ell+1} \otimes U_2$, $U_{2\ell+1} \supset SO_3$ and

$U_2 \supset SU_2$. Indeed, the correspondence between (10) and (11) yields

$$
\begin{aligned}
(\{1^{N-2}\}[f'][\tilde{f}'] + \{1^2\}[f_0][\tilde{f}_0]|\{1^N\}[f][\tilde{f}]) &= \sqrt{\frac{n_{f'}n_{f_0}}{n_f}} \\
([f']\alpha' L' + [f_0]L_0|[f]\alpha L) &= (\ell^N[f]\alpha L\{|\ell^{N-2}[f']\alpha' L', \ell^2[f_0]L_0) \qquad (12) \\
([\tilde{f}']S' + [\tilde{f}_0]S_0|[\tilde{f}]S) &= (s^N[\tilde{f}]S\{|s^{N-2}[\tilde{f}']S', s^2[\tilde{f}_0]S_0).
\end{aligned}
$$

In equations (10) and (12), it is clear that $n_{f_0} = 1$ for both IRC's $[f_0] = [2]$ and $[f_0] = [11]$ of S_2. In the case $[f_0] = [2]$ only even values $L_0 = 0, 2, \cdots, 2\ell$ are admissible and $S_0 = 0$ while for $[f_0] = [11]$ we have $L_0 = 1, 3, \cdots, 2\ell - 1$ and $S_0 = 1$. Furthermore in view of (12), the spin part $(s^N[\tilde{f}]S\{|s^{N-2}[\tilde{f}']S', s^2[\tilde{f}_0]S_0)$ of the fractional-parentage coefficient (10) is trivial in the atomic case since the isoscalar factor $([\tilde{f}']S' + [\tilde{f}_0]S_0|[\tilde{f}]S)$ for the chain $U_2 \supset SU_2$ is unity for the allowed values of S' and S_0. By combining equations (8) to (12), we obtain

$$
\begin{aligned}
{}^{2S+1}E_{\mathrm{av}}[n\ell^N] &= \frac{1}{2}\, N(N-1)\, \frac{1}{N_f} \sum_{\alpha L} \sum_{\alpha' L'} \sum_{S'} \sum_{L_0} \sum_{S_0} \\
&\quad \frac{n_{f'}}{n_f}\, (2L+1)\, (n\ell^2 L_0 S_0|V_{12}|n\ell^2 L_0 S_0)\, |([f']\alpha' L' + [f_0]L_0|[f]\alpha L)|^2.
\end{aligned} \tag{13}
$$

An important step is now to effectuate the summations over αL and $\alpha' L'$ in (13). This may be easily done by using the orthogonality-completeness relation (22) (see appendix) applied to the (orbital) isoscalar factors for the chain $U_{2\ell+1} \supset SO_3$. We thus get

$$
\begin{aligned}
{}^{2S+1}E_{\mathrm{av}}[n\ell^N] &= \frac{1}{2}\, N(N-1) \sum_{S'} \sum_{L_0} \sum_{S_0} \\
&\quad \Delta([f]|[f'] \otimes [f_0])\, \frac{n_{f'}}{n_f}\, \frac{1}{N_{f_0}}\, (2L_0+1)\, (n\ell^2 L_0 S_0|V_{12}|n\ell^2 L_0 S_0).
\end{aligned} \tag{14}
$$

By introducing in (14) the average energy

$$
{}^{2S_0+1}E_{\mathrm{av}}[n\ell^2] = \frac{1}{N_{f_0}} \sum_{L_0} (2L_0+1)\, (n\ell^2 L_0 S_0|V_{12}|n\ell^2 L_0 S_0) \tag{15}
$$

for the configuration $n\ell^2$, we finally arrive at

$$
\begin{aligned}
{}^{2S+1}E_{\rm av}[n\ell^N] \;=\; \frac{1}{2}\,N(N-1) \sum_{S' \text{ or } [f']} \sum_{S_0 \text{ or } [f_0]} \\
{}^{2S_0+1}E_{\rm av}[n\ell^2]\;\Delta([f]|[f']\otimes[f_0])\;\frac{n_{f'}}{n_f}.
\end{aligned}
\tag{16}
$$

Equation (16) provides us with a closed form expression for the N-electron average energy ${}^{2S+1}E_{\rm av}[n\ell^N]$ as a function of the two-electron average energy ${}^{2S_0+1}E_{\rm av}[n\ell^2]$ in the case of a general spin-independent two-body interaction.

At this stage, it is convenient to use the (Σ,Δ)-parametrization defined by (2). In this parametrization, the energy ${}^{2S+1}E_{\rm av}[n\ell^N]$ is a linear combination of the parameters Σ and Δ. The coefficient of Σ in this linear combination is clearly $(1/2)N(N-1)$. Since the parameter Δ appears only in the singlets of $n\ell^2$, the coefficient of Δ in ${}^{2S+1}E_{\rm av}[n\ell^N]$ is $(1/2)N(N-1)(n_{\bar f}/n_f)$, where $n_{\bar f}$ refers to the Young pattern $[\bar f]$ deduced from $[f]$ by omiting its first row. (The latter assertion follows from the fact that $S_0=0$ for the singlet states so that $S'=S$ and thus the sum on $[f']$ in (16) reduces to the orbital Young pattern $[\bar f]$ associated to the spin Young pattern $[\bar\varphi]\equiv[\varphi_1-1,\varphi_2-1]$ for the spin S and the number of electrons $N-2$.) Therefore, equation (16) may be written in the form

$$
{}^{2S+1}E_{\rm av}[n\ell^N] \;=\; \frac{1}{2}\,N(N-1)\left(\Sigma+\frac{n_{\bar f}}{n_f}\Delta\right). \tag{17}
$$

The final step is to calculate the ratio $n_{\bar f}/n_f$ of the dimensions of the IRC's $[\bar f]$ (for S_{N-2}) and $[f]$ (for S_N). This may be achieved by using the well-known formula (see for instance Pauncz 1979) for the IRC's of the symmetric group. We thus get

$$
\frac{n_{\bar f}}{n_f} \;=\; \frac{\varphi_2(\varphi_1+1)}{N(N-1)}. \tag{18}
$$

The introduction of (4) and (18) into (17) leads to equation (1). This completes the proof of the formula (1) for ${}^{2S+1}E_{\rm av}[n\ell^N]$ in the general case of a spin-independent two-body

Hamiltonian. If we are interested in the special case where V is the repulsive Coulomb interaction (ie, $V_{ij} = e^2/r_{ij}$), it is then sufficient to replace the parameters Σ and Δ in (1) by the appropriate linear combinations of the Slater-Condon-Shortley parameters $F^{(k)}$.

3. Appendix: Sum rules for coupling coefficients

Let G be a finite or compact group. We use g to denote an IRC of G and μ to classify the rows and columns of a (standard) unitary matrix representation D^g associated to g. In this notation, the Clebsch-Gordan coefficients of the group G are written $(g_1 g_2 \mu_1 \mu_2 | g_1 g_2 b g \mu)$ where b is an internal multiplicity label to be used when the Kronecker product $g_1 \otimes g_2$ contains the IRC g several times. The Clebsch-Gordan coefficients of G satisfy ordinary unitarity relations controled by summations on $\mu_1 \mu_2$ or $bg\mu$ (see for example Sviridov and Smirnov 1977 and Kibler 1979). In addition, they satisfy the following sum rule (referred to as an orthogonality-completeness relation (Kibler 1979))

$$\sum_{\mu_1} \sum_{\mu} (g_1 g_2 \mu_1 \mu_2 | g_1 g_2 b g \mu)^* \, (g_1 g_2' \mu_1 \mu_2' | g_1 g_2' b' g \mu) = \Delta(g|g_1 \otimes g_2) \, \delta(g_2', g_2) \, \delta(\mu_2', \mu_2) \, \delta(b', b) \, \frac{\dim g}{\dim g_2} \tag{19}$$

where $\Delta(g|g_1 \otimes g_2)$ is 1 or 0 according to as g is contained in $g_1 \otimes g_2$ or not. In the special case where G is the group SU_2 (or SO_3), there is no need for the label b and we have $g \equiv j$ (or ℓ) and $\mu \equiv m_j$ (or m_ℓ) ; in this case, equation (19) is a simple rewriting of one of the two ordinary unitarity relations for the Clebsch-Gordan coefficients $(j_1 j_2 m_1 m_2 | j_1 j_2 j m)$ that follows by using the symmetry property of the latter coefficients under the interchange $j_2 \leftrightarrow j$.

Let us now consider a subgroup H of G. The label μ may then be replaced by the triplet $ah\gamma$, where h stands for an IRC of the group H, γ for an index to characterise

the rows and columns of a (standard) unitary matrix representation D^h associated to h, and a for an external multiplicity label to be used when the IRC h of H occurs several times in the reduction of the IRC g of G. In the $G \supset H$ basis, equation (19) may be transcribed as

$$\sum_{a_1 h_1 \gamma_1} \sum_{a h \gamma} (g_1 g_2 a_1 h_1 \gamma_1 a_2 h_2 \gamma_2 | g_1 g_2 b g a h \gamma)^* \, (g_1 g_2' a_1 h_1 \gamma_1 a_2' h_2' \gamma_2' | g_1 g_2' b' g a h \gamma) = \\ \Delta(g|g_1 \otimes g_2) \, \delta(g_2', g_2) \, \delta(a_2', a_2) \, \delta(h_2', h_2) \, \delta(\gamma_2', \gamma_2) \, \delta(b', b) \, \frac{\dim g}{\dim g_2}. \tag{20}$$

The orthogonality-completeness relation (20) can be rewritten in terms of isoscalar factors for the chain $G \supset H$. For this purpose, we use the Racah factorisation lemma (Racah 1949)

$$(g_1 g_2 a_1 h_1 \gamma_1 a_2 h_2 \gamma_2 | g_1 g_2 b g a h \gamma) = \sum_{\beta} (g_1 a_1 h_1 + g_2 a_2 h_2 | b g a \beta h) \, (h_1 h_2 \gamma_1 \gamma_2 | h_1 h_2 \beta h \gamma) \tag{21}$$

that gives an expression of a Clebsch-Gordan coefficient of G, in a $G \supset H$ basis, as a linear combination of Clebsch-Gordan coefficients $(h_1 h_2 \gamma_1 \gamma_2 | h_1 h_2 \beta h \gamma)$ of H. The coefficients of this linear combination are the isoscalar factors $(g_1 a_1 h_1 + g_2 a_2 h_2 | b g a \beta h)$ for the chain $G \supset H$. (In equation (21), the label β is a multiplicity label of type b.) Then, by applying twice (21) in (20) and by using (19) for the group H in the so-obtained equation, we end up with

$$\sum_{a_1 h_1} \sum_{a h} \sum_{\beta} \frac{\dim h}{\dim h_2} \, (g_1 a_1 h_1 + g_2 a_2 h_2 | b g a \beta h)^* \, (g_1 a_1 h_1 + g_2' a_2' h_2 | b' g a \beta h) = \\ \Delta(g|g_1 \otimes g_2) \, \delta(g_2', g_2) \, \delta(a_2', a_2) \, \delta(b', b) \, \frac{\dim g}{\dim g_2}. \tag{22}$$

Equation (22) constitutes an orthogonality-completeness relation for the isoscalar factors of the chain $G \supset H$.

4. Closing remarks

The unusual sum rule (22) is of central importance in the derivation of the main results (equations (16) and (1)) of this paper. This sum rule is based on (19) and on the Racah lemma. It is interesting to mention that equation (19) also plays a fundamental role in the derivation of sum rules for the intensity of two-photon transitions between Stark levels of a transition ion in a liquid or crystal environment (Kibler and Daoud 1993).

Equation (1) has been derived in the framework of atomic spectroscopy. Let us mention that the result (1) is also of relevance in the spectroscopy of partly-filled shell ions in condensed matter as far as S may be assumed to be a good quantum number (an assumption that is reasonable for transition-metal ions in crystals).

Finally, let us observe that formulas which parallel (16) and (1) might be derived in the shell model of nuclear physics. In this connection, we may think of obtaining average energies for fixed spin S, or fixed isospin T, or fixed spin S and isospin T. However, a complication arises when replacing N electrons on a $n\ell$-atomic shell by N nucleons on a $n\ell$-nuclear shell because the isospin degree of freedom manifests itself by the replacement of the *trivial* spin chain $(U_2)_S \supset (SU_2)_S$ by the *nontrivial* spin-isospin chain $(U_4)_{ST} \supset (U_2 \to SU_2)_S \otimes (U_2 \to SU_2)_T$ (cf Jahn and van Wieringen 1951). We hope to return on this extension to nuclear physics in a forthcoming paper.

Acknowledgment

The present work was began during a stay of one of the authors (Yu F S) in Lyon-Villeurbanne. The latter author acknowledges the *Institut de Physique Nucléaire de Lyon* for the kind hospitality extended to him.

References

Diercksen G H F and Karwowski J 1987 *Comput. Phys. Comm.* **47** 83

Jahn H A and van Wieringen H 1951 *Proc. Roy. Soc.* **A 209** 502

Karwowski J and Bancewicz M 1987 *J. Phys. A: Math. Gen.* **20** 6309

Karwowski J, Valdemoro C and Lain L 1989 *Phys. Rev.* A **39** 4967

Kibler M R 1975 *Int. J. Quantum Chem.* **9** 421

Kibler M R 1979 *Recent Advances in Group Theory and Their Application to Spectroscopy* ed J C Donini (New York: Plenum) p 1

Kibler M and Daoud M 1993 *to be published*

Kibler M and Katriel J 1990 *Phys. Lett.* **147A** 417

Kibler M and Partensky A 1991 *Symmetry and Structural Properties of Condensed Matter* ed W Florek, T Lulek and M Mucha (Singapore: World Scientific) p 251

Neudatchin V G and Smirnov Yu F 1968 *Nucleon Clusters in Light Nuclei* (Moscow: Nauka) (in Russian)

Pauncz R 1979 *Spin Eigenfunctions - Construction and Use* (New York: Plenum)

Racah G 1943 *Phys. Rev.* **63** 367

Racah G 1949 *Phys. Rev.* **76** 1352

Racah G 1951 *Group Theory and Spectroscopy* (Princeton: Institute for Advanced Study)

Sviridov D T and Smirnov Yu F 1977 *Theory of Optical Spectra of Transition-Metal Ions* (Moscow: Sciences) (in Russian)

M.S.
I.D. No.
NAME
RN TO FERMILAB LIBRARY