
By Takahiko YAMANOUCHI.

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§ 1. The energy expressions of an atom or an ion for a configuration containing few electrons outside an almost closed shell are simple notwithstanding the large number of electrons that are taken into account, and the rule for finding them by Slater's method making explicit use of spin eigenfunctions was given by Shortley(1). It is possible, however, to arrive at these expressions more rapidly by group-theoretical or vector-model method, which require purely formal calculations, and seems to be more suitable in some case, for complex configurations especially. In this paper, the latter method is applied for configurations in which a core with an incomplete shell is found in a definite multiplet state, and one inequivalent electron is added to it. Some simple interval rules for the terms of highest multiplicity arising from the configurations containing p and d electrons are obtained, and they are tested by comparison with the experimental values. The generalisation for the case that the core contains other electrons besides the almost closed shell, or more than two electrons are added to such a core is immediate, though the latter has no practical interest.

§ 2. The simplification for the present problem is based on the following property of the closed shell. Suppose that the core consists of a complete shell of electrons of the azimuthal quantum number l', 2(2l'+1)=c in number, and let the eigenfunctions corresponding to l to -l' of magnetic quantum numbers, each of which is contained twice, be represented by $\phi$. Then when another inequivalent electron in a state $n(l, m)$ is added to it, the increase of energy is given, omitting common term for all m, by(2)

$$2 \sum_{\lambda} J_{\lambda} - \sum_{\lambda} K_{\lambda}, \quad (1)$$

where $J_{\lambda}$ and $K_{\lambda}$ are the usual Coulomb and exchange integrals between the electrons $\lambda$ and $n$. Owing to the spherically symmetric

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charge distribution of the core, however, this term is also independent of \( m \), that is, it has the same value for all (spatially degenerated) eigenfunctions of the added electron\(^3\).

§ 3. Now consider a configuration that the core consisting of \( n' = n - 1 \) equivalent electrons is found in a definite multiplet state with the resultant spin \( S' \), and an inequivalent electron is added to it. To find the energies of the states arising from this configuration by the method of sums, we calculate the diagonal elements of the energy matrix for all possible sets of \( n \) eigenfunctions, which are characterised by their magnetic quantum numbers. Let the eigenfunctions of core electron contained twice in the set be denoted by \( \alpha \), and those contained once by \( i \), and that of the added electron by \( n \), as in the former paper\(^3\). Then the sum of the energies for the states \( S = S' \pm \frac{1}{2} \) is given, apart from terms common to \( m \), by\(^4\)

\[
g' \left( 2 \sum J_{an} + \sum J_{in} - \sum K_{an} + \zeta \sum K_{in} \right),
\]

where \( g' \) is the dimension of the irreducible representation of the symmetric group \( S_{n-2p-1} \) corresponding to the resultant spin \( S' \) of the core, \( p \) is the number of the eigenfunctions \( \alpha \) contained twice in the set, and\(^5\)

\[
\zeta = -(S'/n' + 1/2) \quad \text{for} \quad S = S' + 1/2,
\]

\[
= (S' + 1)/n' - 1/2 \quad \text{for} \quad S = S' - 1/2.
\]

The formula (2) is not convenient for practical use, since the number \( p \) is large for an almost closed shell, and hence we must find large number of terms \( J_{an} \) and \( K_{an} \). To reduce this into simpler form, let us introduce the eigenfunctions \( \beta \) that are not contained in the set. \( \alpha \), \( i \), and \( \beta \) correspond then, by suitable rearrangement, to \( l' \) to \(-l'\). The formula (2) can be written in the form:

\[
g' \left[ 2 \left( \sum J_{an} + \sum J_{in} + \sum J_{\beta n} \right) - \left( \sum K_{an} + \sum K_{in} + \sum K_{\beta n} \right) \right] - \left( 2 \sum J_{\beta n} - \sum J_{in} + \sum K_{\beta n} + (1 + \zeta) \sum K_{in} \right).\]

The first two sums of the bracket is equal to \( 2 \sum J_{an} - \sum K_{an} \), which is independent of the particular choice of \( n \) (§ 2). Hence, the above sum of the energies is expressed in an alternative form:

\[\text{(3) Analytical proof is given in Condon-Shortley, (1), § 9, p. 177.}\]
\[\text{(4) l.c. (2), 826, formula (14).}\]
\[\text{(5) l.c. (2), 825, formula (8) and (9).}\]
\[ \text{const.} + g' \left| -2 \sum J_{\beta M_n} - \sum J_{\alpha n} + \sum K_{\beta a} + (1 + \xi) \sum K_{\alpha a} \right|, \quad (3) \]

which is preferable than (2), since the number of \( \beta \) is always less than \( \alpha \).

§ 4. The formula (3) shows resemblance to the corresponding expression for the case that \( n'' = c - n' \) core electrons are present, so that we can find the energies by considering holes of the almost closed shell. We shall next find what kinds of holes \( \beta, i \) are to be taken for the sets with \( \sum m' + m = M \), since to make use the method of sums, the sets are selected for each possible values of \( M \). When \( m \) has a definite value, \( m' = M' \) must also be fixed. On the other hand, the sum of \( m' \) for all states in a closed shell is zero: \( \sum m'_s + \sum m'_i + \sum m'_p = 0 \). Consequently, \( \sum m_i + 2 \sum m_p = -M' \). Thus we obtain the rule. Select the sets of \( n'' = c - n' \) eigenfunctions which make \( \sum m' = M' \). Then reversing the signs of each \( m' \), we get the eigenfunctions of the holes which make \( \sum m' = M' \) for the almost closed shell configuration. Let \( \beta \) and \( i \) be the eigenfunctions contained twice and once respectively in the set of holes. Then the sum of the energies required is given by (3).

The integral \( J \) is independent of the sign of \( m' \), so that the Coulomb terms are obtained from the corresponding \( n'' + 1 \) electron problem by merely changing the signs. Exchange terms, on the contrary, are much changed, and simpler in general, since \( G_s \) for different signs of \( (m', m) \) is often zero.

If the core contains other electrons besides the almost closed shell, we have only to add the energies between these and added electrons, where \( g' \) and \( \xi \) are, of course, to be taken for the resultant state of the core.

§ 5. We shall illustrate the method by a simple example \( d^s p \). Omitting \( m' \) for \( s \)-electron which is zero, we have the following sets for respective values of \( M \):

| \( d^p \) | \( m_i, m_p \) | \( (2, 1) \) | \( (2, 0); (1, 1) \) | \( (3, -1); (1, 0); (0, 1) \) |
| \( d^p \) | \(-m_i, m_p \) | \( (-2, 1) \) | \( (-2, 0); (-1, 1) \) | \( (-3, -1); (-1, 0); (0, 1) \) |

The energies of the terms arising from \( ^3D \) and \( ^1D \) states of the core are then found by taking the differences of the sums of the energies calculated by (3) for successive \( M \).

\[ (^3D) L = -J_L - G' \]
\[ (^1D) L = -J_L \frac{1}{2} G' + \frac{3}{2} K_L \]
where \( L = F, D, P, G^* = G'(sp) \), and

\[
\begin{align*}
J_F &= -2F, \\
J_D &= 7F, \\
J_P &= -2F, \\
K_F &= 45G, \\
K_D &= 0, \\
K_P &= 10G.
\end{align*}
\]

These terms are observed in Cu I. \( 3d^44s^1 \). From the differences of \( 4F - 4P \) and \( 4D - 4P \), we obtain nearly equal values of \( F_2 = 323 \) and \( 316 \). From the differences of the doublet terms arising from \( 1D \), \( G_1 = 261 \) and \( G_3 = 124 \), and from the difference of \( 4D \) and \( 2D \), \( G_2 = 1533 \) are obtained. The terms arising from \( 1D \) of the core are then calculated by these parameter values, but the comparison with experimental values is difficult owing to the large multiplet separations and strong perturbations from \( 3d^{10}mp \), so that these values of \( G \) are not confirmed. Nevertheless, these are not improbable estimates, since \( F_2 = 351 \), \( G_1 = 304 \), \( G_3 = 12 \) for \( 3d^34p^1 \), and \( G^* = 2006 \) for \( 3d^34s \) of Cu II.

§ 6. For the highest multiplet states, \( g' = 1 \) and \( \zeta = -1 \), so that the coefficient of \( \sum K_{1m} \) is 0. Also the eigenfunctions of the holes must all be different. Therefore, all the exchange terms vanish if the core consists of an almost closed shell only, and simple interval rules are obtained if each term \( (L, S) \) arises once and the Coulomb parts are expressed in small number of \( F's \). For \( pp \) and \( pd \), only one parameter \( F \) is contained for the differences of these terms, and the ratios of the intervals can be predicted. They are tabulated below contrasted to the observed values.

Also when the core contains \( s \) electrons besides the incomplete shell, both Coulomb and exchange terms are equal for all \( m \) of the added electron, and disappear in the differences of energies of the same multiplet. Similar interval rules are therefore obtained for them, which are included in the table.

\[
\begin{align*}
\frac{4S^* - 4P}{2} &= 5 \\
\frac{4D^* - 4P}{2} &= 2.5 \text{ cm}^{-1}.
\end{align*}
\]

(6) Term values (in \( \text{cm}^{-1} \)) are taken from Bacher-Goudsmith, Atomic Energy States. The centers of gravity of the multiplets are determined as the mean with the weights \( 2J+1 \) for each term \( J \).


(8) I wish in this occasion to correct the mistake in my paper, Proc. Phys.-Math. Soc. Japan, III, 18, 10 (1933). The coefficients of \( F_2 \) on page 21 should be 1, -5, 10: 1, -5, 10 (equal to \( -J \) of \( pp \)). With this correction the following regular values of \( F_2 \), \( G_1 \), and \( G_3 \) are obtained for \( 3p^23p \) configurations:
<table>
<thead>
<tr>
<th>configuration</th>
<th>(2p^2 , 3p)</th>
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<tbody>
<tr>
<td>F I</td>
<td>Ne II</td>
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<tr>
<td>ratio</td>
<td>2'12</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>configuration</th>
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<tbody>
<tr>
<td>Cl I</td>
<td>A II</td>
</tr>
<tr>
<td>ratio</td>
<td>2'43</td>
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</tbody>
</table>

\[ p'd. \quad \frac{\epsilon P - \epsilon D}{\epsilon F - \epsilon D} = \frac{14}{9} = 1.56. \]

<table>
<thead>
<tr>
<th>configuration</th>
<th>(3p^4 , 3d)</th>
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<tr>
<td>Ne II</td>
<td>A II</td>
</tr>
<tr>
<td>ratio</td>
<td>1.38</td>
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</tbody>
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<table>
<thead>
<tr>
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<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
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<tbody>
<tr>
<td>element</td>
<td>C I*</td>
<td>N I</td>
<td>O I</td>
<td>F I</td>
<td>Ne I**</td>
</tr>
<tr>
<td>(F_f)</td>
<td>150</td>
<td>147</td>
<td>153</td>
<td>158</td>
<td>167</td>
</tr>
<tr>
<td>(G_a)</td>
<td>1382</td>
<td>1140</td>
<td>(1000)</td>
<td>851</td>
<td>751</td>
</tr>
<tr>
<td>(G_a)</td>
<td>26.4</td>
<td>36.2</td>
<td>(47)</td>
<td>53</td>
<td>44.8</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>element</th>
<th>N II*</th>
<th>O II***</th>
<th>F II</th>
<th>Ne II</th>
<th>Na II***</th>
</tr>
</thead>
<tbody>
<tr>
<td>(F_f)</td>
<td>397</td>
<td>373</td>
<td>378</td>
<td>428</td>
<td>444</td>
</tr>
<tr>
<td>(G_a)</td>
<td>3007</td>
<td>2265</td>
<td>3102</td>
<td>2203</td>
<td>2000</td>
</tr>
<tr>
<td>(G_a)</td>
<td>111</td>
<td>79</td>
<td>77</td>
<td>169</td>
<td>150</td>
</tr>
</tbody>
</table>

* Calculated from the term values determined by B. Edlén, Zeit. f. Phys. 84, 748 (1933).
** G. H. Shortley, Phys. Rev. 47, 295 (1935), Table III, A and B.
**** Determined by similar method as in (7).
For O I \(2p^4(3S)3p\), using the rough interpolated values in the brackets, we get \(\epsilon P - \epsilon F = 43/10 G_a = 1960\) (observed 2001). These regularities are to be compared to those for \(\epsilon^*\), H. A. Robinson and G. H. Shortley, Phys. Rev. 52, 713 (1937).
(9) Term values are taken from J. Söderqvist, Nova Acta Reg. Soc. Sc. Upsal, IX, 7, 1 (1934).
The orders of the terms are all given correctly, but the observed ratios are generally smaller than the calculated. This is particularly the case for the deep-lying configurations. It is generally observed that among the energies of deep-lying configurations, the energy of the lowest term is calculated too high in first order approximation. In some of the above examples, it may also to a part be attributed to the insufficient elimination of the energies due to the spin-orbit interactions, which act in unique sense to lower the all terms \( J \) for the deepest state. The abnormal value for Mn I may be due to the perturbation from the configuration \( 3d^{3}4s4p \).

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