Energy Levels of the Electron Configuration \( p^2p' \).

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(Read February 19, 1938)

§ 1. The energy levels of the states \((L, S)\), which arise once from a given electron configuration, can be expressed linearly in relatively small number of parameters \( F_k \) and \( G_k \) by the well known method of Slater\(^{(1)}\). But for those states \((L, S)\) arising more than once, only the sums of their energies are known by that method, and to find them separately, we have to solve the secular equations for the Hamiltonian, whose elements are given by\(^{(2)}\)

\[
H_{ij} = \sum_{s} u_{ik}(s) H(s|AB),
\]

in which \( p \) is the number of paired orbitals, \( u_{ik}(s) \) is the representation matrix of an element \( s \) of the symmetric group. The summation extends, besides the unit element \( I \), for all the elements \( s \) interchanging different orbitals. In the following, this method is applied for the configuration \( p^2p' \), and the results are compared with the observed data.

§ 2. The terms arising from \( p^2p' \) are \( ^2P, ^2P, ^2D, ^2F, ^2S, ^2P, ^2D, ^4S, ^4P, ^4D \). By Slater's method, we obtain the following table for the terms that arise once:

**Table of the coefficients of \( F \)'s and \( G \)'s**

\( (F = F(pp), F = F(pp'), G = G(pp')) \)

<table>
<thead>
<tr>
<th></th>
<th>( F'_0 )</th>
<th>( F'_1 )</th>
<th>( F'_2 )</th>
<th>( F'_3 )</th>
<th>( G'_0 )</th>
<th>( G'_1 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( ^2P )</td>
<td>1</td>
<td>-5</td>
<td>2</td>
<td>-1</td>
<td>-1</td>
<td>-4</td>
</tr>
<tr>
<td>( ^2P )</td>
<td>1</td>
<td>-5</td>
<td>2</td>
<td>-10</td>
<td>-10</td>
<td></td>
</tr>
<tr>
<td>( ^2S )</td>
<td>1</td>
<td>-5</td>
<td>2</td>
<td>-10</td>
<td>-10</td>
<td></td>
</tr>
<tr>
<td>( ^2P )</td>
<td>1</td>
<td>2</td>
<td>-10</td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( ^2S )</td>
<td>1</td>
<td>2</td>
<td>-10</td>
<td>2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

We shall find the energies of two \( ^4D \) and three \( ^4P \) terms by constructing the matrix elements of the Hamiltonian for \( \sum_m = M_z = -2 \) and 1, and diagonalising them\(^{(3)}\): \( u_{ik}(s) \) for \( s = 1/2, n = 3 \) are as follows\(^{(3)}\):

\[
\begin{bmatrix}
1 & 0 \\
0 & 1
\end{bmatrix}, \begin{bmatrix}
-1 & 0 \\
0 & 1
\end{bmatrix}, \begin{bmatrix}
1/2 & -\sqrt{3}/2 \\
\sqrt{3}/2 & -1/2
\end{bmatrix}, \begin{bmatrix}
1/2 & \sqrt{3}/2 \\
\sqrt{3}/2 & 1/2
\end{bmatrix}.
\]

(1) J. C. Slater, Phys. Rev. 34, 1933 (1939).
(3) The approximate expression neglecting the interactions of the states arising from different parent terms \( ^2P, ^4D, ^4S \) of \( p^2 \) are given by T. Yamanouchi, Proc. Phys.-Math. Soc. Japan, III, 18, 10 (1936).
§ 3. For $M_L=2$, the wave functions characterised by the magnetic quantum numbers $m_i$ of individual electrons are

$$A=(1, 0, 1'), \quad B=(1, 1, 0'),$$

which give rise to the terms $^2F, ^2D, ^2D$. By the table of Condon and Shortley, The Theory of Atomic Spectra, pp. 179, we find:

$$H(1|A,A)=J(1, 0)+J(1, 1')+J(0, 1')=1$$

$$H(1|A,A)=K(1, 0)$$

$$H(1|A,A)=K(1, 1')$$

$$H(1|B,B)=K(1, 1)+2J(1, 0')=-1$$

$$H(1|B,B)=K(1, 0')$$

$$H(1|A,B)=K(1, 0')$$

$$H(1|A,B)=(01'; 10')$$

Thus we obtain the following matrix elements for the Hamiltonian:

$$H=F_0+2F_0' + S$$

$$S=\begin{pmatrix}
-5 & -1 & 1/2 & 2 \\
0 & 0 & 1 & -2 \\
1 & -1 & -1/2 & -2 \\
0 & 0 & 6 & -1 \\
1 & -4 & 0 & -3
\end{pmatrix}$$

where in the brackets are given the coefficients of $F_0, F_0', G_0, G_3$ in this order. We omit the lower left parts of matrix $S$, since it is symmetric.

$^2F$ and the diagonal elements of two $^2D$ for a particular scheme characterised by the parent terms being known, $S$ must be transformed by a unitary transformation to the form:

$$R=\begin{pmatrix}
1 & 2 & -1 & -1 \\
0 & 0 & 0 & 0 \\
1 & -1 & 1/2 & -4 \\
1 & -1 & 1/2 & 2
\end{pmatrix}$$

$$R=U^*SU, \quad U^*U=1, \quad U=(a_{1k}), \quad (a_{1k})$$

Comparing the (1, 1)-element of (2), and equating the coefficients of $F_0$'s and $G_0$'s, we get

$$a_{11}=0, \quad a_{11}=\sqrt{2}a_{11}.$$
again by unitary condition, we obtain the transformation matrix:

\[
U = \begin{pmatrix}
1\frac{3}{\sqrt{5}} & \frac{1}{\sqrt{5}} & \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{3}} \\
\frac{1}{\sqrt{3}} & 1 & -\frac{1}{\sqrt{5}} & -\frac{1}{\sqrt{2}} \\
\frac{1}{\sqrt{5}} & -\frac{1}{\sqrt{2}} & 1 & -\frac{1}{\sqrt{3}} \\
\frac{1}{\sqrt{2}} & \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{5}} & 1
\end{pmatrix}
\]

and \(S\) is brought to the form:

\[
R = \begin{pmatrix}
(1, 2, -1, -1) & 0 & 0 \\
(1, -7, 1/2, -4) & -3/2 (0, 0, 1, -2) \\
(-5, 1/2, 2) & (3)
\end{pmatrix}
\]

§ 4. \(M_z = 1\). The terms contained are \(^2F, ^2D, ^2P, ^4P, ^4P\), and the wave functions are

\(A = (1, 1, -1'), B = (1, 0, 0'), C = (1, -1, 1'), D = (0, 0, 1').\)

By the similar calculations as before, we get

\[
S = H - F_0 - 2F_0^2
\]

The transformed part of \(S\) for \(^2F, ^2D, ^2D\) (3), and the diagonal elements of \(^4P, ^4P, ^4P\) are known\(^n\), so that \(S\) is to be transformed into the form:

\[
U^*SU = R = \begin{pmatrix}
(1, 2, -1, -1) & 0 & 0 \\
(-5, 1/2, 2) & -3/2 (0, 0, 1, -2) \\
(1, -7, 1/2, -4)
\end{pmatrix}
\]

By similar but a little laborious calculation as in the preceding paragraph, we find:
§ 5. Comparison with the experimental data.

For comparison, we take 0 II. The parameter values are determined from \(4D, 4P, 4S, 4S, 4P, \) and \(\Sigma D\) by least squares:

\[
\begin{align*}
U &= \begin{pmatrix}
1/\sqrt{15} & 0 & 1/\sqrt{5} & 0 & \sqrt{3}/5 & 0 \\
0 & 1/\sqrt{2} & 0 & 1/\sqrt{2} & 0 & 0 \\
-2\sqrt{2}/15 & 0 & -1/\sqrt{6} & 0 & \sqrt{3}/10 & 0 \\
0 & -1/\sqrt{2} & 0 & 1/\sqrt{2} & 0 & 0 \\
\sqrt{3}/15 & 0 & -1/\sqrt{6} & 0 & \sqrt{2}/3 & \sqrt{3}/3 \\
-2/\sqrt{15} & 0 & 1/\sqrt{3} & 0 & -1/\sqrt{15} & 1/\sqrt{3}
\end{pmatrix}
\end{align*}
\]

and

\begin{align*}
\pi &= \sqrt{5}/2 (0, 12, -1, -1), \\
y &= -(0, 0, 1, -6), \\
z &= (\sqrt{5}/2 (0, 0, 1, 4).
\end{align*}

The calculated values of the terms, those of \(4D, 4D,\) and \(4P, 4P, 4P\) being found by solving quadratic and cubic equations respectively, contrasted to the observed values are shown in following table.

\[
\begin{array}{|c|c|c|c|c|}
\hline
P_0 + 2P'_0 & P_0 & P'_0 & G_0 & G_2 \\
\hline
55302 & 3443 & 378 & 3102 & 77 \\
\hline
\end{array}
\]

In conclusion, I wish to express my cordial thanks to Prof. T. Yamanouchi for suggesting this problem, and to Prof. M. Kotani for kind guidance throughout the work.

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(Received February 19, 1938)