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Theory of Complex Spectra

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A method for the calculation of the energy levels of an atom in terms of the experimentally observed energy levels of ions of higher ionization is developed. This method can be applied to a system of nonequivalent electrons, as well as equivalent electrons. The notion of fractional parentage is extended to systems of nonequivalent electrons. Tables of fractional parentage coefficients are calculated for p^2s, p^3s, and d^2p configurations. Application is made by a least-squares calculation of the $3d^24p$ configuration of Ti II in terms of the experimentally observed energies of the $3d^2$ and $3d4p$ configurations of Ti III. As a result, the root-mean-square deviation of our calculated values from the experimental energies is reduced to ± 249 cm^{-1}.

I. INTRODUCTION

In this paper we shall consider the efficacy of trying to express the energies of any ion or atom in terms of the experimentally observed energies of ions of higher ionization. This approach was first taken by Goudsmit and Bacher[1] using a method based on a diagonal sum procedure, and restricting themselves to configurations involving s and p electrons. Their method expresses the energy of an atom in terms of the observed energies of the ions of higher ionization. The accuracy of their results increases with the amount of experimental data available. For best results, the observed energies of all ionizations must be used. In our method, knowledge of only the next higher ion energies is necessary. It should be noted that if the energies of only the next lower ion are known, our method is still valid. In Sec. II, we shall make use of the tensor operator methods developed by Racah[2-4] and shall not restrict ourselves to s and p electrons.

Inasmuch as we would like to treat configurations involving nonequivalent electrons as well as those involving equivalent electrons, we shall in Sec. III extend the idea of fractional parentage, which was also first introduced by Goudsmit and Bacher,[1] and was developed by Racah.[3] Racah calculated fractional parentage only for equivalent electron configurations. We shall show that the method of calculation can be extended to include nonequivalent electrons as well. We shall calculate coefficients for p^2s, p^3s, and d^2p configurations. In Sec. IV, a d^2p calculation involving the methods of Secs. II and III will be discussed in detail inasmuch as it is a prototype for other calculations of this type. Since Racah has derived the expressions for the matrices of the d^2p configuration for Ti II and has also made a calculation of the predicted energy levels, we have a good check available on the proposed method. Our method leads to better agreement with experiment in the calculation of the energy levels since the root-mean-square deviation of the calculated energies from the experimental ones is ± 249 cm^{-1} as compared to the ± 332 cm^{-1} obtained by Racah. Although our method improves upon the results obtained by Racah, it should be noted that his method involves the use of only four parameters instead of the five used here, and the use of the experimental energies of d^2 only.

II. ENERGIES OF ATOMS IN TERMS OF OBSERVED ENERGIES OF HIGHER IONS

In treating complex spectra it is customary to express the energy of a term as a function of various F_k and G_k radial integrals.[5,6] These integrals are usually treated as parameters which can be calculated from the observed values of energies. Of course, any one integral, say F_0 or F_2, varies from configuration to configuration.

We assume that the F_k's and G_k's of any configuration can be written in terms of the F_k's and G_k's of the next higher configuration as follows:

$$F_k(l^n)=F_k(l^{n-1})+\Delta F_k,\quad G_k(l^n)=G_k(l^{n-1})+\Delta G_k. \tag{1}$$

Let us consider the d^2 and d^3 configurations. From TAS[6] we can write $W(d^3)$, the energy of any term of the d^3 configuration as a function of the radial integrals F_k. We assume that the F_k's of the d^3 configuration can be written in terms of the F_k's of the d^2 configuration as follows:

$$\begin{aligned}F_k(d^3)&=F_k(d^2)+\Delta F_k,\\ F_0(d^3)&=F_0(d^2)+\Delta F_0,\\ F_2(d^3)&=F_2(d^2)+\Delta F_2,\\ F_4(d^3)&=F_4(d^2)+\Delta F_4.\end{aligned} \tag{1-a}$$

Therefore, the energy of the $d^3\ {}_3{}^4P$ term is

$$\begin{aligned}W(d^3\ {}_3{}^4P)&=3F_0(d^3)-147F_4(d^3)\\ &=3F_0(d^2)-147F_4(d^2)+3\Delta F_0-147\Delta F_4.\end{aligned} \tag{2}$$

We should like to express $3F_0(d^3)-147F_4(d^3)$ in terms

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

[2] G. Racah, Phys. Rev. **62**, 438 (1942), referred to as R-II.

[3] G. Racah, Phys. Rev. **63**, 367 (1943), referred to as R-III.

[4] G. Racah, Phys. Rev. **76**, 1352 (1949), referred to as R-IV.

[5] J. C. Slater, Phys. Rev. **34**, 1293 (1929).

[6] E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, Cambridge, 1951), referred to as TAS.

of experimental observations for d^2. Equation (1) of R-IV is

$$
\begin{aligned}
&(l^n\alpha SL|G|l^n\alpha' SL)\\
&\quad=\frac{n}{n-2}\sum_{\alpha_1\alpha_1'S_1L_1}(l^n\alpha SL[\![l^{n-1}(\alpha_1S_1L_1)lSL)\\
&\qquad\times(l^{n-1}\alpha_1S_1L_1|G|l^{n-1}\alpha_1'S_1L_1)\\
&\qquad\qquad\times(l^{n-1}(\alpha_1'S_1L_1)lSL]\!]l^n\alpha' SL),\qquad(3)
\end{aligned}
$$

where we can consider G to be the electrostatic interaction. The above equation expresses the energies of an n-electron configuration as a linear combination of energies of an $(n-1)$ electron configuration.

Using Table II of R-III for the values of the fractional parentage coefficients for the calculation of the ${}_3{}^4P$ term of d^3, and noting that $n/(n-2)=3$, (3) gives

$$W(d^3\,{}_3{}^4P)=(3/15)[8W({}_2{}^3P)+7W({}_2{}^3F)],\qquad(4)$$

where $W({}_2{}^3P)$ and $W({}_2{}^3F)$ are energies of the two-electron configuration. Expressing $8W({}_2{}^3P)+7W({}_2{}^3F)$ in terms of F_k's,[7]

$$W(d^3\,{}_3{}^4P)=3F_0-147F_4,\qquad(5)$$

where F_0 and F_4 that are written here are the F's of (d^3) because all of the electrons we are considering here are d^3 electrons. We have really expressed the energy of ${}_3{}^4P$ as a linear combination of the energies of pairs of d^3 electrons. We can therefore write (5) in the form of (2). If we now write $(3/15)[8W(d^2\,{}_2{}^3P)+7W(d^2\,{}_2{}^3F)]$ in terms of the F's of d^2, we find that

$$\tfrac{1}{5}[8W(d^2\,{}_2{}^3P)+7W(d^2\,{}_2{}^3F)]=3F_0(d^2)-147F_4(d^2).\qquad(6)$$

So it is possible to write $W(d^3\,{}_3{}^4P)$ in terms of the experimentally observed energies of d^2 plus a linear combination of parameters which represents the change in value of the radial integrals as we go from one configuration to the next lower configuration,

$$
\begin{aligned}
W(d^3\,{}_3{}^4P)=(8/5)W(d^2\,{}_2{}^3P)+(7/5)W(d^2\,{}_2{}^3F)&\\
+3\Delta F_0-147\Delta F_4.&\qquad(7)
\end{aligned}
$$

To calculate the energy levels of d^3 in terms of the experimentally observed energies of d^2, the equations are

$$
\begin{aligned}
&W(d^3\,{}_3{}^2P)=(1/10)[7W(d^2\,{}_2{}^3P)+15W(d^2\,{}_2{}^1D)\\
&\quad+8W(d^2\,{}_2{}^3F)]+3\Delta F_0-6\Delta F_2-12\Delta F_4,\\
&W(d^3\,{}_3{}^4P)=(1/5)[8W(d^2\,{}_2{}^3P)+7W(d^2\,{}_2{}^3F)]\\
&\quad+3\Delta F_0-147\Delta F_4,\\
&W(d^3\,{}_3{}^2F)=(3/70)[28W(d^2\,{}_2{}^3P)+10W(d^2\,{}_2{}^1D)\\
&\quad+7W(d^2\,{}_2{}^3F)+25W(d^2\,{}_2{}^1G)]+3\Delta F_0+9\Delta F_2-87\Delta F_4,\\
&W(d^3\,{}_3{}^4F)=(3/5)[W(d^2\,{}_2{}^3P)+4W(d^2\,{}_2{}^3F)]\\
&\quad+3\Delta F_0-15\Delta F_2-72\Delta F_4,\\
&W(d^3\,{}_3{}^2G)=(1/14)[10W(d^2\,{}_2{}^1D)+21W(d^2\,{}_2{}^3F)\\
&\quad+11W(d^2\,{}_2{}^1G)]+3\Delta F_0-11\Delta F_2+13\Delta F_4,\qquad(8)\\
&W(d^3\,{}_3{}^2H)=(3/2)[W(d^2\,{}_2{}^3F)+W(d^2\,{}_2{}^1G)]\\
&\quad+3\Delta F_0-6\Delta F_2-12\Delta F_4,\\
&W(d^3\,{}_1{}^2D)^{*}\text{[8]}=(1/20)[16W(d^2\,{}_0{}^1S)+9W(d^2\,{}_2{}^3P)\\
&\quad+5W(d^2\,{}_2{}^1D)+21W(d^2\,{}_2{}^3F)+9W(d^2\,{}_2{}^1G)]\\
&\quad+3\Delta F_0+7\Delta F_2+63\Delta F_4,\\
&W(d^3\,{}_3{}^2D)^{*}=(3/140)[49W(d^2\,{}_2{}^3P)+45W(d^2\,{}_2{}^1D)\\
&\quad+21W(d^2\,{}_2{}^3F)+25W(d^2\,{}_2{}^1G)]\\
&\quad+3\Delta F_0+3\Delta F_2-57\Delta F_4.
\end{aligned}
$$

To find the off-diagonal element, we apply (3),

$$
\begin{aligned}
&W(d^3\,{}_{1,3}{}^2D)=(3/(60\cdot 140)^{\frac12})[21W(d^2\,{}_2{}^3P)\\
&\qquad-15W(d^2\,{}_2{}^1D)-21W(d^2\,{}_2{}^3F)+15W(d^2\,{}_2{}^1G)]\\
&\qquad\qquad+3(21)^{\frac12}[\Delta F_2-5\Delta F_4].\qquad(9)
\end{aligned}
$$

TABLE I. Coefficients of fractional parentage for d^2p.

				d^2						dp		
d^2p	N	${}_0{}^1S$	${}_2{}^3P$	${}_2{}^1D$	${}_2{}^3F$	${}_2{}^1G$	${}^1P$	${}^1D$	${}^1F$	${}^3P$	${}^3D$	${}^3F$
${}^2S$	$6^{-\frac12}$		$2^{\frac12}$					$3^{\frac12}$			1	
${}^4S$	$3^{-\frac12}$		1								$2^{\frac12}$	
${}^4P$	$90^{-\frac12}$		$30^{\frac12}$							$-27^{\frac12}$	$5^{\frac12}$	$-28^{\frac12}$
${}^4F$	$15^{-\frac12}$		$5^{\frac12}$							$-2^{\frac12}$	$5^{\frac12}$	$3^{\frac12}$
${}^4G$	3^{-1}				$3^{\frac12}$						1	$-5^{\frac12}$
${}^2H$	$6^{-\frac12}$					$2^{\frac12}$			1			$-3^{\frac12}$
${}^4D$	$150^{-\frac12}$		$50^{\frac12}$							3	$-35^{\frac12}$	$56^{\frac12}$
${}^4D$	$75^{-\frac12}$				$25^{\frac12}$					$28^{\frac12}$	$20^{\frac12}$	$2^{\frac12}$
${}^2G$	6^{-1}				$12^{\frac12}$			$-3^{\frac12}$	$15^{\frac12}$		-1	$5^{\frac12}$
${}^2G$	6^{-1}					$12^{\frac12}$		$-5^{\frac12}$	-1		$15^{\frac12}$	$3^{\frac12}$
${}^2P$	$90^{-\frac12}$	$30^{\frac12}$					$-3^{\frac12}$	$5^{\frac12}$	$-7^{\frac12}$	3	$-15^{\frac12}$	$21^{\frac12}$
${}^2P$	$360^{-\frac12}$		$120^{\frac12}$				-9	$15^{\frac12}$	$84^{\frac12}$	$-54^{\frac12}$	$5^{\frac12}$	$28^{\frac12}$
${}^2P$	$360^{-\frac12}$			$120^{\frac12}$			$-21^{\frac12}$	$-35^{\frac12}$	-2	$63^{\frac12}$	$105^{\frac12}$	$12^{\frac12}$
${}^2D$	$600^{-\frac12}$		$200^{\frac12}$				$27^{\frac12}$	$-105^{\frac12}$	$168^{\frac12}$	3	$-35^{\frac12}$	$56^{\frac12}$
${}^2D$	$120^{-\frac12}$			$40^{\frac12}$			$7^{\frac12}$	$-5^{\frac12}$	$-8^{\frac12}$	$-21^{\frac12}$	$15^{\frac12}$	$24^{\frac12}$
${}^2D$	$150^{-\frac12}$				$50^{\frac12}$		$42^{\frac12}$	$30^{\frac12}$	$3^{\frac12}$	$14^{\frac12}$	$10^{\frac12}$	1
${}^2F$	$210^{-\frac12}$			$70^{\frac12}$			-1	$10^{\frac12}$	$-24^{\frac12}$	$3^{\frac12}$	$-30^{\frac12}$	$72^{\frac12}$
${}^2F$	$60^{-\frac12}$				$20^{\frac12}$		$-6^{\frac12}$	$15^{\frac12}$	3	$-2^{\frac12}$	$5^{\frac12}$	$3^{\frac12}$
${}^2F$	$420^{-\frac12}$					$140^{\frac12}$	$-54^{\frac12}$	$-15^{\frac12}$	-1	$162^{\frac12}$	$45^{\frac12}$	$3^{\frac12}$

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[7] R-II, Eqs. (77) and (78).

[8] * denotes diagonal element.

III. FRACTIONAL PARENTAGE FOR NONEQUIVALENT ELECTRONS

A. Theoretical Foundation

In R-III, Racah develops a formalism to obtain antisymmetric eigenfunctions when coupling equivalent electrons only. We want to couple n electrons, none of which are equivalent, or more important, two or more of which are equivalent, in such a way as to yield antisymmetric eigenfunctions.

Let us build a wave function for a three-electron configuration. This can be done by coupling electron 1 with electron 2 and then coupling the system $(1+2)$ with electron 3. This process must yield the same result as coupling electron 2 with electron 3 and then coupling the system $(2+3)$ with electron 1,

$$\psi(l_1l_2(S'L')l_3SL)=\sum_{S''L''}\psi(l_1,\,l_2l_3(S''L''),\,SL)\times(l_1,\,l_2l_3(S''L''),\,SL|l_1l_2(S'L')l_3SL),\qquad(10)$$

where the transformation matrix is given by

$$\begin{aligned}(s_1l_1s_2l_2(S'L')s_3l_3SL|s_1l_1,\,s_2l_2s_3l_3(S''L''),\,SL)&=[(2S'+1)(2S''+1)(2L'+1)(2L''+1)]^{\frac{1}{2}}\\&\times W(s_1s_2Ss_3;\,S'S'')W(l_1l_2Ll_3;\,L'L'').\qquad(11)\end{aligned}$$

We obtain in general in (10) both allowed and forbidden values of $S''L''$. Those values of $S''L''$ that are forbidden are the ones denoting states represented by symmetric eigenfunctions. Therefore

$$\psi(l_1l_2(S'L')l_3SL)$$

is not always an eigenfunction of $l_1l_2l_3$. The proper eigenfunction of $l_1l_2l_3$ is a linear combination,

$$\Psi(l_1l_2l_3\alpha SL)=\sum_{S'L'}\psi(l_1l_2(S'L')l_3SL)\times(l_1l_2(S'L')l_3SL]\!]l_1l_2l_3\alpha SL)\qquad(12)$$

in which the coefficients of $\psi(\mathbf{l}_1,\,l_2l_3(S''L''),\,S\mathbf{L})$ vanish for all forbidden $S''L''$ after application of (10). We call $(l_1l_2(S'L')l_3SL]\!]l_1l_2l_3\alpha SL)$ coefficients of fractional parentage. These coefficients must satisfy the system of equations:

$$\sum_{S'L'}(l_1,\,l_2l_3(S''L''),\,SL|l_1l_2(S'L')l_3SL)\times(l_1l_2(S'L')l_3SL]\!]l_1l_2l_3\alpha SL)=0,\qquad(13)$$

for all forbidden $S''L''$, i.e., if l_2 and l_3 are equivalent electrons, $S''+L''$ must be odd.

We can extend this method to configurations $l_1l_2\cdots l_{n-1}l_n$ if fractional parentages of $l_1l_2\cdots l_{n-1}$ are known.

$$\begin{aligned}\Psi(l_1\cdots l_n\alpha SL)&=\sum_{\alpha'S'L'}\psi(l_1\cdots l_{n-1}(S'L')l_nSL)\\&\quad\times(l_1\cdots l_{n-1}(\alpha'S'L')l_nSL]\!]l_1\cdots l_n\alpha SL)\\&=\sum_{\alpha'S'L'\alpha''S''L''}\psi(l_1\cdots l_{n-2}(\alpha''S''L'')l_{n-1}(S'L')l_nSL)\\&\quad\times(l_1\cdots l_{n-2}(\alpha''S''L'')l_{n-1}S'L']\!]l_1\cdots l_{n-1}\alpha'S'L')\\&\quad\times(l_1\cdots l_{n-1}(\alpha'S'L')l_nSL]\!]l_1\cdots l_n\alpha SL),\qquad(14)\end{aligned}$$

where the coefficients of fractional parentage,

$$(l_1\cdots l_{n-1}(\alpha'S'L')l_nSL]\!]l_1\cdots l_n\alpha SL),$$

must satisfy the system of equations:

$$\begin{aligned}\sum_{\alpha'S'L'}&(S''L'',\,l_{n-1}l_n(S'''L'''),\,SL|S''L''l_{n-1}(S'L')l_nSL)\\&\times(l_1\cdots l_{n-2}(\alpha''S''L'')l_{n-1}S'L']\!]l_1\cdots l_{n-1}\alpha'S'L')\\&\times(l_1\cdots l_{n-1}(\alpha'S'L')l_nSL]\!]l_1\cdots l_n\alpha SL)=0,\qquad(15)\end{aligned}$$

for all forbidden $S'''L'''$; i.e., for l_{n-1}, l_n equivalent, $S'''+L'''$ must be equal to 0.

We can write an equation similar to (3) for the energy of a term of a configuration of nonequivalent electrons,

$$\begin{aligned}(l_1\cdots l_n\alpha SL|G|l_1\cdots l_n\alpha'SL)&=\binom{n}{n-2}\sum_{\alpha\alpha_1'S_1L_1}(l_1\cdots l_n\alpha SL[\![l_1\cdots l_{n-1}(\alpha_1S_1L_1)l_nSL)\\&\quad\times(l_1\cdots l_{n-1}\alpha_1S_1L_1|G|l_1\cdots l_{n-1}\alpha_1'S_1L_1)\\&\quad\times(l_1\cdots l_{n-1}(\alpha_1'S_1L_1)l_nSL]\!]l_1\cdots l_n\alpha'SL).\qquad(16)\end{aligned}$$

TABLE II. Coefficients of fractional parentage for p^2s.

			p^2		ps	
p^2s	N	${}^1S$	${}^3P$	${}^1D$	${}^1P$	${}^3P$
${}^2S$	$6^{-\frac{1}{2}}$	$2^{\frac{1}{2}}$			1	$-3^{\frac{1}{2}}$
${}^2P$	$6^{-\frac{1}{2}}$		$2^{\frac{1}{2}}$		$3^{\frac{1}{2}}$	1
${}^4P$	$3^{-\frac{1}{2}}$		1			$2^{\frac{1}{2}}$
${}^2D$	$6^{-\frac{1}{2}}$			$2^{\frac{1}{2}}$	1	$-3^{\frac{1}{2}}$

B. Calculation of Coefficients of Fractional Parentage of d^2p

To illustrate the method, let us calculate the eigenfunction of $d^2p\ {}^2S$,

$$\begin{aligned}\Psi(d^2p\ {}^2S)=\theta_1\psi((d^2\ {}_2{}^3P)p\ {}^2S)&+\gamma_1\psi((dp\ {}^1D)d\ {}^2S)\\&+\lambda_1\psi(dp\ {}^3D)d\ {}^2S),\qquad(17)\end{aligned}$$

where θ_1, γ_1, λ_1 are coefficients of fractional parentage to be determined. Applying (13)[9] and using $dd({}^1P)$ as the unallowed state, with

$$\begin{array}{llllll}s_3=\frac{1}{2}, & s_2=\frac{1}{2}, & s_1=\frac{1}{2}, & S=\frac{1}{2}, & S'=0, & S''=0,1\\ l_3=1, & l_2=2, & l_1=2, & L=0, & L'=1, & L''=2,2\end{array}\qquad(18)$$

we find that $-\frac{1}{2}\gamma_1+\frac{1}{2}\sqrt{3}\lambda_1=0$.

$$\gamma_1=\sqrt{3}\lambda_1.\qquad(19)$$

Since our eigenfunction is to be normalized

$$\theta_1^2+\gamma_1^2+\lambda_1^2=1=\theta_1^2+4\lambda_1^2.\qquad(20)$$

It then becomes necessary to fix the contribution of the the terms in d^2 and in dp to the energy of the ${}^2S$ state of d^2p. Since the three electrons d, d, p can be grouped into d^2, dp, dp we say that the dp states contribute

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[9] The W functions are mostly taken from L. C. Biedenharn, Oak Ridge National Laboratory Report ORNL-1098 (unpublished).

TABLE III. Coefficients of fractional parentage for p^3s.

p^3s	N	p^3			p^2s			
		^4S	^2P	^2D	^2S	^2P	^4P	^2D
^3S	$12^{-\frac{1}{2}}$	$3^{\frac{1}{2}}$				$8^{\frac{1}{2}}$	$3^{\frac{1}{2}}$	
^5S	$2^{-\frac{1}{2}}$	1					1	
^1P	$24^{-\frac{1}{2}}$		$6^{\frac{1}{2}}$		-2	-3		$5^{\frac{1}{2}}$
^3P	$24^{-\frac{1}{2}}$		$6^{\frac{1}{2}}$		-2	1	$-8^{\frac{1}{2}}$	$5^{\frac{1}{2}}$
^1D	$8^{-\frac{1}{2}}$			$2^{\frac{1}{2}}$		$3^{\frac{1}{2}}$		$3^{\frac{1}{2}}$
^3D	$24^{-\frac{1}{2}}$			$6^{\frac{1}{2}}$		1	$-8^{\frac{1}{2}}$	$-3^{\frac{1}{2}}$

twice as much as the d^2 state. Therefore

$$\theta_1^2=\tfrac{1}{3}, \tag{21}$$

$$\theta_1=3^{-\frac{1}{2}},\quad \lambda_1=6^{-\frac{1}{2}},\quad \gamma_1=2^{-\frac{1}{2}}, \tag{22}$$

$$\Psi(d^2p\,^2S)=(3^{-\frac{1}{2}})\psi(d^2\,{}_2{}^3P)p\,^2S)+(2^{-\frac{1}{2}})\psi((dp\,^1D)d\,^2S)+(6^{-\frac{1}{2}})\psi((dp\,^3D)d\,^2S). \tag{23}$$

It should be noted that when calculating the coefficients in the case of, say $\Psi(d^2p\,^2D)$, where we have a 3×3 matrix, each diagonal element is characterized by having a particular d^2 term among its parents. Consider the element having $d^2({}_2{}^3P)$ among its parents. In addition to having $dd(^1P)$, $dd(^3D)$, and $dd(^1F)$ as unallowed states, where the two d electrons are equivalent, we also consider $d^2({}_2{}^1D)$ and $d^2({}_2{}^3F)$ (both being parents of the other two diagonal elements) as unallowed states. For the element having $d^2({}_2{}^1D)$ among its parents, in addition to having $dd(^1P)$, $dd(^3D)$, and $dd(^1F)$ as unallowed states, we also consider $d^2({}_2{}^3P)$ and $d^2({}_2{}^3F)$ as unallowed states. For the element having $d^2({}_2{}^3F)$ among its parents, the unallowed states are $dd(^1P)$, $dd(^3D)$, $dd(^1F)$, $d^2({}_2{}^3P)$, and $d^2({}_2{}^1D)$. Our formalism will then yield the proper number of equations to evaluate all of the coefficients. In general, when treating states with two or more diagonal elements, the unallowed states are those arising from the symmetric states of the higher ion plus the equivalent electron sources of the diagonal elements different from the one at hand. Table I lists all of the coefficients of fractional parentage for the d^2p configuration. Table II lists the coefficients for the p^2s configuration.

C. Calculation of Coefficients of Fractional Parentage of p^3s

To illustrate a calculation involving more than three electrons, consider the calculation of $\Psi(p^3s\,^3S)$. We shall make use of the coefficients of fractional parentage of p^2s listed in Table II.

$$\Psi(p^3s\,^3S)=\alpha\psi(p^3(^4S)s\,^3S)+\beta\psi(p^2s(^4P)p\,^3S)+\gamma\psi(p^2s(^2P)p\,^3S), \tag{24}$$

α, β, γ are coefficients of fractional parentage to be determined. We expand the eigenfunctions of $\psi(p^3\,^4S)$, $\psi(p^2s\,^4P)$, $\psi(p^2s\,^2P)$.

$$\begin{aligned}\Psi(p^3s\,^3S)={}&\alpha\cdot1\cdot\psi(p^2(^3P)p(^4S)s\,^3S)\\&+\beta(\sqrt{2}/\sqrt{3})\psi(ps(^3P)p(^4P)p\,^3S)\\&+\beta(1/\sqrt{3})\psi(pp(^3P)s(^4P)p\,^3S)\\&+\gamma(1/\sqrt{2})\psi(ps(^1P)p(^2P)p\,^3S)\\&+\gamma(1/6^{\frac{1}{2}})\psi(ps(^3P)p(^2P)p\,^3S)\\&+\gamma(1/\sqrt{3})\psi(pp(^3P)s(^2P)p\,^3S).\end{aligned} \tag{25}$$

TABLE IV. The elements of the energy matrices of the configuration d^2p. The use of this table is illustrated by writing the energy of the $d^2p\,^2S$ term. $W(d^2(^3P)\,^2S)=W(d^2\,^3P)+\frac{3}{2}W(dp\,^1D)+\frac{1}{2}W(dp\,^3D)+\Delta A+7\Delta B-14\Delta F_2-3\Delta G_1+21\Delta G_3$.

d^2p	N	d^2	dp												Core
			^1P	^1D	^1F	^3P	^3D	^3F	ΔA	ΔB	ΔC	ΔF_2	ΔG_1	ΔG_3	(cm^{-1})
$W(d^2(^3P)\ ^2S)$	1	$W(^3P)$	0	3/2	0	0	1/2	0	1	7	0	−14	−3	21	162 084
$W(d^2(^3P)\ ^4S)$	1	$W(^3P)$	0	0	0	0	2	0	1	7	0	−14	6	−42	165 168
$W(d^2(^3P)\ ^4P)$	1	$W(^3P)$	0	0	0	9/10	1/6	14/15	1	7	0	7	−6	−63	169 080
$W(d^2(^3F)\ ^4F)$	1	$W(^3F)$	0	0	0	2/5	1	3/5	1	−8	0	−3	−1	−48	156 597
$W(d^2(^3F)\ ^4G)$	1	$W(^3F)$	0	0	0	0	1/3	5/3	1	−8	0	1	−9	−12	155 736
$W(d^2(^1G)\ ^2H)$	1	$W(^1G)$	0	0	1/2	0	0	3/2	1	4	2	4	−6	−3	172 725
$W(d^2(^3P)\ ^4D)$	1	$W(^3P)$	0	0	0	9/50	7/10	28/25	1	7	0	−7/5	−24/5	−147/5	166 503
$W(d^2(^3F)\ ^4D)$	1	$W(^3F)$	0	0	0	28/25	4/5	2/25	1	−8	0	12/5	4/5	−438/5	158 977
$W(d^2(^3P,\,^3F)\ ^4D)$	$3(14)^{\frac{1}{2}}/5$	0	0	0	0	1/5	−1/3	2/15	0	0	0	4	−2	−6	1853
$W(d^2(^3F)\ ^2G)$	1	$W(^3F)$	0	1/4	5/4	0	1/12	5/12	1	−8	0	1	9/2	6	161 811
$W(d^2(^1G)\ ^2G)$	1	$W(^1G)$	0	5/12	1/12	0	5/4	1/4	1	4	2	−11	3/2	−18	168 685
$W(d^2(^3F,\,^1G)\ ^2G)$	$(15)^{\frac{1}{2}}/2$	0	0	1/6	−1/6	0	−1/6	1/6	0	0	0	0	−3	6	−2365
$W(d^2(^1S)\ ^2P)$	1	$W(^1S)$	1/10	1/6	7/30	3/10	1/2	7/10	1	14	7	0	−2	−21	193 618
$W(d^2(^3P)\ ^2P)$	1	$W(^3P)$	27/40	1/8	7/10	9/40	1/24	7/30	1	7	0	7	3	63/2	174 410
$W(d^2(^1D)\ ^2P)$	1	$W(^1D)$	7/40	7/24	1/30	21/40	7/8	1/10	1	−3	2	−3	1	−69/2	165 739
$W(d^2(^1S,\,^3P)\ ^2P)$	$(3)^{\frac{1}{2}}$	0	3/20	1/12	−7/30	−3/20	−1/12	7/30	0	0	0	0	−3	21	−1697
$W(d^2(^1S,\,^1D)\ ^2P)$	$(7)^{\frac{1}{2}}$	0	1/20	−1/12	1/30	3/20	−1/4	1/10	0	0	0	4	−1	−3	3474
$W(d^2(^3P,\,^1D)\ ^2P)$	$(21)^{\frac{1}{2}}/2$	0	3/20	−1/12	−1/15	−3/20	1/12	1/15	0	0	0	0	0	15	553
$W(d^2(^3P)\ ^2D)$	1	$W(^3P)$	27/200	21/40	21/25	9/200	7/40	7/25	1	7	0	−7/5	12/5	147/10	170 231
$W(d^2(^1D)\ ^2D)$	1	$W(^1D)$	7/40	1/8	1/5	21/40	3/8	3/5	1	−3	2	3	−2	−57/2	167 355
$W(d^2(^3F)\ ^2D)$	1	$W(^3F)$	21/25	3/5	3/50	7/25	1/5	1/50	1	−8	0	12/5	−2/5	219/5	160 420
$W(d^2(^3P,\,^1D)\ ^2D)$	$3(7)^{\frac{1}{2}}/(15)^{\frac{1}{2}}$	0	3/40	1/8	−1/5	−3/40	−1/8	1/5	0	0	0	0	−3	27/2	−2255
$W(d^2(^3P,\,^3F)\ ^2D)$	$3(14)^{\frac{1}{2}}/10$	0	3/10	−1/2	1/5	1/10	−1/6	1/15	0	0	0	8	2	6	5137
$W(d^2(^1D,\,^3F)\ ^2D)$	$3/(30)^{\frac{1}{2}}$	0	7/10	−1/2	−1/5	−7/10	1/2	1/5	0	0	0	0	2	66	1063
$W(d^2(^1D)\ ^2F)$	1	$W(^1D)$	1/70	1/7	12/35	3/70	3/7	36/35	1	−3	2	−6/7	−23/7	−69/7	165 559
$W(d^2(^3F)\ ^2F)$	1	$W(^3F)$	3/10	3/4	9/20	1/10	1/4	3/20	1	−8	0	−3	1/2	24	158 270
$W(d^2(^1G)\ ^2F)$	1	$W(^1G)$	27/70	3/28	1/140	81/70	9/28	3/140	1	4	2	55/7	−3/14	−372/7	175 582
$W(d^2(^1D,\,^3F)\ ^2F)$	$(3)^{\frac{1}{2}}/(7)^{\frac{1}{2}}$	0	1/10	1/2	−3/5	−1/10	−1/2	3/5	0	0	0	0	−10	30	−2559
$W(d^2(^1D,\,^1G)\ ^2F)$	$3(3)^{\frac{1}{2}}/7$	0	1/10	−1/6	1/15	3/10	−1/2	1/5	0	0	0	8	−2	−6	1949
$W(d^2(^3F,\,^1G)\ ^2F)$	$3/(28)^{\frac{1}{2}}$	0	3/5	−1/2	−1/10	−3/5	1/2	1/10	0	0	0	0	3	54	1240

Our condition on β and γ is

$$\beta(\sqrt{2}/\sqrt{3})[ps({}^3P),\, pp({}^1P)\,{}^3S|ps({}^3P)p({}^4P)p\,{}^3S] +\gamma(6^{-\frac{1}{2}})[ps({}^3P),\, pp({}^1P)\,{}^3S|ps({}^3P)p({}^2P)p\,{}^3S]=0. \quad (26)$$

From (15) we obtain (26), the brackets of which may be put in the form of (11), where

$$\begin{aligned} &s_3=1, \quad s_2=\tfrac{1}{2}, \quad s_1=\tfrac{1}{2}, \quad S=1, \quad S'=0, \quad S''=\tfrac{3}{2}, \tfrac{1}{2}, \\ &l_3=1, \quad l_2=1, \quad l_1=1, \quad L=0, \quad L'=1, \quad L''=1, 1. \end{aligned} \quad (27)$$

Therefore

$$\gamma=2\sqrt{2}\beta, \quad (28)$$

and, as before,

$$\alpha^2+\beta^2+\gamma^2=1=\alpha^2+9\beta^2. \quad (29)$$

To fix the relative contributions of p^3 and p^2s to p^3s, we consider the four electrons $ppps$. There are three ways to get p^2s out of the four electrons, as opposed to one way to get p^3. We therefore say that the p^2s states make three times the contribution of the p^3 state. Therefore

$$\alpha^2=\tfrac{1}{4}, \quad \alpha=\tfrac{1}{2}, \quad \beta=1/(2\sqrt{3}), \quad \gamma=\sqrt{2}/\sqrt{3}, \quad (30)$$

$$\Psi(p^3s\,{}^3S)=(\tfrac{1}{2})\psi(p^3({}^4S)s\,{}^3S)+[1/(2\sqrt{3})]\psi(p^2s({}^4P)p\,{}^3S) +(\sqrt{2}/\sqrt{3})\psi(p^2s({}^2P)p\,{}^3S). \quad (31)$$

Table III lists the coefficients of fractional parentage of p^3s.

TABLE V. Values of parameters. All parameters have units of cm^{-1}.

	Approximate	Perturbation	Final[a]
ΔA	$-126\,989$	273	$-126\,716$
ΔB	-35.7	-0.5	-36.2
ΔC	76.8	-225.2	-148.4
ΔF_2	-177.7	19.2	-158.5
ΔG_1	-108.7	25.2	-83.5
ΔG_3	-12.32	4.15	-8.17

[a] Final value is the sum of the approximate value and the perturbation.

IV. CALCULATION OF THE $3d^24p$ CONFIGURATION OF Ti II

We shall calculate the term values for the $3d^24p$ configuration of Ti II in terms of the experimentally observed energies of $3d^2$ and $3d\,4p$ of Ti III. To find the energy of any element we apply (16). We arrive at equations which, when written in terms of F_k's and G_k's, are similar to those of R-II, except that our coefficient of G_3 is three times that of Racah's, since we used the G_3 of TAS. However, if we wish to write the terms in terms of experimentally observed energies of $3d^2$ and $3d\,4p$, and in terms of F_k's and G_k's, we obtain equations like

$$W(d^2p\,{}^2H)=W(d^2\,{}_2{}^1G)+\tfrac{1}{2}W(dp\,{}^1F)+\tfrac{3}{2}W(dp\,{}^3F) +\Delta A+4\Delta B+2\Delta C+4\Delta F_2-6\Delta G_1-3\Delta G_3, \quad (32)$$

where ΔA includes the change in the A of the d^2 configuration and the change in the F_0 of the dp configuration; ΔB and ΔC refer to changes in the B and C of the d^2 configuration; and ΔF_2, ΔG_1, ΔG_3 refer to changes in the F_2, G_1, and G_3 of the dp configuration. All of the levels written in this form are listed in Table IV. The terms of dp and d^2 are taken from the U. S. Tables.[10] The sums of the observed energies, or the "experimental cores," are also listed in Table IV.

TABLE VI. Energies of the $3d^24p$ configuration of Ti II. All numbers are in units of cm^{-1}.

Term	Experiment	Racah	Δ_1[a]	Calculated	Δ_2[b]
$({}^3P)\,{}^2S$	37 431	37 628	+197	37 413	− 18
$({}^3P)\,{}^4S$	40 027	40 237	+210	40 260	+233
$({}^3P)\,{}^4P$	42 127	42 100	− 27	42 018	−109
$({}^3F)\,{}^4F$	31 108	31 125	+ 17	31 123	+ 15
$({}^3F)\,{}^4G$	29 936	29 823	−113	30 001	+ 65
$({}^1G)\,{}^2H$	45 802	45 184	−618	45 459	−343
$({}^3P)\,{}^4D$	40 612	40 441	−171	40 506	−106
$({}^3F)\,{}^4D$	32 690	32 890	+200	32 711	+ 21
$({}^3F)\,{}^2G$	34 657	34 109	−548	34 175	−482
$({}^1G)\,{}^2G$	43 763	43 675	− 88	43 721	− 42
$({}^3P)\,{}^2D$	44 907	44 737	−170	44 897	− 10
$({}^1D)\,{}^2D$	39 380	40 000	+620	39 928	+548
$({}^3F)\,{}^2D$	31 918	32 251	+333	32 003	+ 85
$({}^1D)\,{}^2F$	40 011	39 507	−504	39 662	−349
$({}^3F)\,{}^2F$	31 369	31 471	+102	31 387	+ 18
$({}^1G)\,{}^2F$	47 535	48 078	+543	47 801	+266
$({}^1S)\,{}^2P$	···	64 465	···	66 060	···
$({}^3P)\,{}^2P$	45 524	45 673	+149	45 814	+290
$({}^1D)\,{}^2P$	39 627	39 496	−131	39 321	−306
rms deviation			±332		±249

[a] Δ_1 is the deviation of Racah's calculated value from experiment.
[b] Δ_2 is the deviation of the value calculated in this paper from experiment.

A least-squares calculation to determine the value of parameters ΔA, ΔB, ΔC, ΔF_2, ΔG_1, and ΔG_3 is carried out using the equations in Table IV. At this stage in the calculation, the $d^2p\,{}^2P$ matrix is not included due to the uncertainty of $W(d^2\,{}_0{}^1S)$. The parameters obtained as a result of this calculation are listed in Table V. In order to bring into the calculation the effect of each of the separate terms of the ${}^4D$, ${}^2G$, ${}^2D$, and ${}^2F$ matrices, we use a perturbation procedure given by Many[11] and Rohrlich.[12] The changes in parameters obtained in this way are listed in Table V, as are the final values of these parameters. The eigenvalues, obtained using the parameters listed in Table V, are listed, together with the results obtained by Racah, in Table VI. Our values for the ${}^2P$ terms are calculated using the parameters of Table V and using a value of $W(d^2\,{}_0{}^1S)$ computed from the parameters of Cady.[13] The value of $W(d^2\,{}_0{}^1S)$ listed in the U. S. Tables is not used, since in a calculation for Ti II d^3 from the observed energies of Ti III d^2, large discrepancies occurred due to its use.

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[10] C. E. Moore, "Atomic Energy Levels," Natl. Bur. Standards U. S. Circ. 467 (1949).

[11] A. Many, Phys. Rev. **70**, 511 (1946).

[12] F. Rohrlich, Phys. Rev. **74**, 1381 (1948).

[13] W. M. Cady, Phys. Rev. **43**, 322 (1933).

The results obtained show a root-mean-square deviation of ±249 cm^{-1} compared to Racah's ±332 cm^{-1}. Certainly, one more application of the perturbation method and the inclusion of the ^2P matrix in obtaining our normal equations would yield still better values. An error in the calculation of the ^2P terms occurs because of the uncertainty in the value of $W(d^2\,{}_0{}^1S)$.

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Electrostatic Energy Matrices of the Configuration f^4

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The electrostatic energy matrices of the configuration f^4 are computed by the Racah method, which separates terms of the same kind. The diagonal sums of these matrices are checked by the Slater diagonal sum rule. Three of the matrices are checked by a method developed by Innes.

RACAH[1] has developed a method for computing the electrostatic energy matrices of the configuration f^4. This method enables one to separate terms of the same kind which occur in a given configuration, whereas Slater's method[2] finds only the sum, or average, of the terms of the same kind. Hence, the latter method is a partial check on the former. Both methods have been applied to the f^4 configuration and the results of Racah's method are given in Table I. The eigenvalues of the two-by-two matrices are given in Table II. The multiplicity of the term r is the left superscript, the seniority number v is the left subscript, and in place of J, the right subscript, the quantum numbers U have been inserted. These quantum numbers are found in Table I of reference 1, and serve to distinguish terms of the same L, S, and v.

The parameters E^0, E^1, E^2, and E^3 are defined in terms of Slater's F's in reference 1, Eq. (66) as follows:

$$\begin{aligned} E^0 &= F_0-10F_2-33F_4-286F_6,\\ E^1 &= (70/9)F_2+(231/9)F_4+(2002/9)F_6,\\ E^2 &= (1/9)F_2-(1/3)F_4+(7/9)F_6,\\ E^3 &= (5/3)F_2+2F_4-(91/3)F_6. \end{aligned} \tag{1}$$

As a further check on the interpretation of the Racah method, matrix elements for three typical matrices (^1S, a two-by-two matrix, ^3P, a three-by-three matrix, and ^3F, a four-by-four matrix) have been checked by a

TABLE I. Electrostatic energy matrices of the configuration f^4.

$${}_4{}^1F_{21}=6E^0+6E^1-195E^2+33E^3$$

$${}_4{}^1K_{21}=6E^0+6E^1-129E^2-11E^3$$

$${}_4{}^1N_{22}=6E^0+6E^1+60E^2-11E^3$$

$${}_4{}^3L_{21}=6E^0+4E^1-85E^2-19E^3$$

$${}_4{}^3M_{30}=6E^0+4E^1+50E^2-19E^3$$

$${}_4{}^5S_{00}=6E^0$$

$${}_4{}^5D_{20}=6E^0+33E^3$$

$${}_4{}^5F_{10}=6E^0$$

$${}_4{}^5G_{20}=6E^0+12E^3$$

$${}_4{}^5I_{20}=6E^0-21E^3$$

	${}_0{}^1S_{00}$	${}_4{}^1S_{22}$
${}_0{}^1S_{00}$	$6E^0+18E^1$	$-12(22)^{\frac{1}{2}}E^3$
${}_4{}^1S_{22}$	$-12(22)^{\frac{1}{2}}E^3$	$6E^0+6E^1+390E^2+66E^3$

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[1] G. Racah, Phys. Rev. 76, 1352 (1949).

[2] J. C. Slater, Phys. Rev. 34, 1293 (1929).