Introduction

Praseodymium (Pr) is one of the rare Earth elements with a commonly open 4f electron shell. The only stable isotope that occurs naturally, with electronic ground state [Xe] 4f⁵ 6s², 4f⁰ ⁹/₂, nuclear magnetic dipole moment μ₁ = 4.2754(5) μN, nuclear spin quantum number I = ⁵/₂ [1] and nuclear electric quadrupole moment Q = −0.0024b [2]. Pr is very rich in optical spectrum. The major portion of spectrum is in visible green region. That is why in lighting industry, it is of valuable importance [3].

Literature survey reveals that in 1928, King initiated investigations of singly ionized Pr (Pr II) [4]. The frequency separation of fine structure components of 173 spectral lines in Pr II ion was observed by H. White in 1929 [5]. Ginibre made great advancements in classification of Pr II lines and levels until 1989 [6–8]. Investigations of spectral lines of Pr II, published after 1989, were concerned with two features: either the measurements of transition probabilities and life times [9, 10] or accuracy measurements of hyperfine structure constants for the levels already known using laser induced fluorescence (LIF) method in a hollow cathode [11] or on a fast ion beam method [12–18]. Using Laser spectroscopy method, Zeeman structure of 6 lines in the wavelength range 649.5728—669.351 nm was recorded [19]. The structures of 32 spectral lines of Pr I were investigated by LIF spectroscopy. Researchers found Lande g₁ factors for 71 new experimental results [20]. In 1953, H. Lew used magnetic resonance technique to investigate hyperfine structure of ground state of Pr for which total electronic angular momentum, nuclear spin and g J value was calculated. It was observed that ⁴I₃/₂ was Pr’s atomic ground state. Further, he showed that the Russell-Saunders coupling also led to this state in accordance with Hund’s rule—the most stable ground state of 4f⁵ 6s² configuration [21]. In addition to research into Pr as an interesting element in atomic physics, spectral lines of Pr II are also extensively investigated with the perspective of other fields in Physics, especially Astrophysics. Wahlgren [22] and Biemont [23] presented a compilation of status of knowledge of all Lanthanide elements. Term values are used to examine the electronic and magnetic properties of inorganic molecules and complexes and helpful in describing energy, spin multiplicity and angular momentum of an atom/ion for any electronic configuration. The knowledge about spectral and magnetic properties of an atom or ion is provided by Russell-Saunders atomic term symbols. Such
technique was employed to calculate atomic terms for non equivalent electrons \((n - 1) d^s l^p\) configuration for which 120 microstates were computed [24]. Russell Saunders coupling scheme was also used by Meena et al to calculate microstates and term values of \(n^6\) and \(n^6\) configurations which were found to be 1001 and 47 respectively [25].

The objective of present study is to determine the term and angular momentum values and also coupled wave functions for \(4f^2 5d^2\) configuration of Pr-II using Russell-Saunders and coefficient of fractional parentage methods.

**Methodology**

Term values refer to energy states and give information of angular momenta. Atomic terms provide details about magnetic and spectral properties of elements. The number of terms in case of equivalent electrons is lesser in number as compared to that of non-equivalent electrons. Wave functions provide information of allowed values of quantum states and are used to calculate the energy and other radiative properties of states. Term symbols in Russell-Saunders coupling scheme are given in the form of \(^{(2S+1)I}\), where \(S\) denotes the orbital angular momentum, \(L\) takes the spin angular momentum, and \(J\) shows the total angular momentum. In a term symbol, \(L\) takes values 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, ..., with each value of \(L\) being represented by English Capital letters 'S, P, D, F, G, H, I, K, ...'. It is assumed in the Russell-Saunders Scheme that spin–orbit coupling \(<\) orbit–orbit coupling \(<\) spin-spin coupling.

Allowed terms for the configuration \(4f^2 5d^2\) are found by considering equivalent \(f^2\) and \(d^2\). The terms arising from equivalent electron \(f^2\) and \(d^2\) are found by taking Pauli’s Principle into account. Terms of \(f^2\) were used as parent terms of allowed terms of the configuration \(4f^2 5d^2\). Combination rule was applied to combine terms of \(f^2\) and \(d^2\) and to obtain allowed terms of the configuration of interest. To find the characteristic wavefunctions of configuration \(4f^2 5d^2\), necessary data was collected from previous step, coupled wavefunctions and coefficients of fractional parentage were determined [26–28]. A computer program was developed which first found terms of equivalent electrons and then combined them to find allowed terms of configuration; this data is further used by the program to find normalized wavefunctions of the configuration.

**Results and discussion**

The present work gives information about the term values, total angular momentum (J) values and normalized coupled wave functions of \(4f^2 5d^2\) configuration of singly ionized Praseodymium based on Russell-Saunders and coefficient of fractional parentage methods. The electronic configuration \(4f^2 5d^2\) was investigated for fine structure details of Pr II. Total number of allowed atomic spectroscopic terms calculated for this configuration is 187. In 1989, Ginibre determined various parameters of hyperfine and fine structure for low lying configurations of Pr II. The stability order of term schemes was determined by Hund’s rule [26]. In \(4f^2 5d^2\) out of 187 term values, 9 of them are quintets, 10 are triplets and 11 are singlets. Stability order is \(^3L > ^3K > ^3H > ^3G > ^3F > ^3D > ^3P > ^3S > ^3M > ^1L > ^3K > ^1H > ^3H > ^1G > ^1F > ^1D > ^1P > ^1S\). The ground state term for \(4f^2 5d^2\) configuration is quintet \(L(3L)\).

The configuration \(4f^2 5d^2\)

Configuration \(4f^2 5d^2\) is an even configuration of Pr II; this configuration is studied here in detail. The number of LS terms, number of fine levels and corresponding angular momenta, allowed terms, coefficients of fractional parentage and coupled wave functions are determined. This configuration has 187 LS terms and total fine levels belonging to different \(J\) are 457 for \(4f^2 5d^2\) configuration. The levels with \(J = 4\) have maximum frequency. The terms of equivalent electrons \(f^2\) and \(d^2\) were found first. The terms of \(f^2\) were used as parent terms and are combined with the terms of \(d^2\). The angular momenta of combining terms and parents together with the angular momenta of final terms were used to find the coefficients of fractional parentage and wavefunctions of the terms. The coefficient of fractional parentage provides details about anti-symmetric coupled wave functions for allowed term values.

Table 1. List of LS Terms of \(4f^2 5d^2\).

| Terms | \(^3S\) | \(^3P\) | \(^3D\) | \(^3F\) | \(^3G\) | \(^3H\) | \(^3I\) | \(^3K\) | \(^3L\) | \(^3M\) |
|-------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| Quantity | 2 | 4 | 12 | 9 | 13 | 8 | 9 | 4 | 4 | 1 |
| Terms \(5S\) | \(^5P\) | \(^5D\) | \(^5F\) | \(^5G\) | \(^5H\) | \(^5I\) | \(^5K\) | \(^5L\) | \(^5M\) |
| Quantity | 2 | 11 | 12 | 17 | 14 | 14 | 9 | 7 | 3 | 2 |
| Terms \(5S\) | \(^5P\) | \(^5D\) | \(^5F\) | \(^5G\) | \(^5H\) | \(^5I\) | \(^5K\) | \(^5L\) | \(^5M\) |
| Quantity | 2 | 2 | 5 | 4 | 5 | 3 | 3 | 3 | 3 | 1 |

**Sources**

- [24] [25] [26] [27] [28]
Table 2. Designation of fine levels corresponds to 4f² 5d².

| J | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|------|
| Frequency | 21 | 40 | 70 | 71 | 78 | 61 | 52 | 31 | 21 | 8 | 4 | 457 |

Wavefunctions of fine levels of configuration 4f² 5d².

(1I) 1N > = 1[f2d2 1G; (1I) 1N >

(1I) 1M > = 1[f2d2 1G; (1I) 1M >

(1I) 1L > = 0.7866[f2d2 1G; (1I) 1L > + 0.6155[f2d2 1G; (1I) 1L >

(1G) 1L > = 0.7866[f2d2 1G; (1G) 1L > + 0.6155[f2d2 1G; (1G) 1L >

(1I) 1K > = 0.9385[f2d2 1G; (1G) 1K > + 0.3498[f2d2 1G; (1I) 1K >

(1G) 1K > = 0.9385[f2d2 1G; (1G) 1K > + 0.346[f2d2 1G; (1I) 1K >

(1I) 1J > = −0.3949[f2d2 1G; (1I) 1J > − 0.3485[f2d2 1G; (1I) 1J > + 0.853[f2d2 1G; (1I) 1J >

(1G) 1J > = 0.2666[f2d2 1G; (1G) 1J > + 0.8567[f2d2 1G; (1G) 1J > − 0.4938[f2d2 1G; (1I) 1J >

(1I) 1I > = 0.7032[f2d2 1G; (1I) 1I > + 0.3355[f2d2 1G; (1I) 1I > + 0.6269[f2d2 1G; (1I) 1I >

(1H) 1H > = 0.8873[f2d2 1G; (1I) 1H > + 0.4579[f2d2 1G; (1G) 1H > + 0.0553[f2d2 1G; (1I) 1H >

(1I) 1H > = 0.8873[f2d2 1G; (1I) 1H > + 0.4579[f2d2 1G; (1G) 1H > + 0.0553[f2d2 1G; (1I) 1H >

(1G) 1H > = 0.8873[f2d2 1G; (1G) 1H > + 0.4579[f2d2 1G; (1G) 1H > + 0.0553[f2d2 1G; (1I) 1H >

(1I) 1G > = 0.8873[f2d2 1G; (1I) 1G > + 0.4579[f2d2 1G; (1G) 1G > + 0.3943[f2d2 1G; (1I) 1G > + 0.7319[f2d2 1G; (1I) 1G >

(1G) 1G > = 0.5593[f2d2 1G; (1G) 1G > − 0.1801[f2d2 1G; (1I) 1G > + 0.4316[f2d2 1G; (1I) 1G > + 0.7003[f2d2 1G; (1I) 1G >

(1I) 1F > = 0.7269[f2d2 1G; (1I) 1F > + 0.2955[f2d2 1G; (1I) 1F > + 0.3965[f2d2 1G; (1I) 1F > + 0.4765[f2d2 1G; (1I) 1F >

(1I) 1E > = 0.3212[f2d2 1G; (1I) 1E > − 0.8058[f2d2 1G; (1I) 1E > + 0.4975[f2d2 1G; (1I) 1E >

(1G) 1F > = −0.3212[f2d2 1G; (1I) 1F > + 0.8058[f2d2 1G; (1I) 1F > + 0.4975[f2d2 1G; (1I) 1F >

(1I) 1D > = 0.6424[f2d2 1G; (1I) 1D > + 0.4853[f2d2 1G; (1I) 1D > + 0.3946[f2d2 1G; (1I) 1D >

(1G) 1D > = 0.6424[f2d2 1G; (1I) 1D > + 0.4853[f2d2 1G; (1I) 1D > + 0.3946[f2d2 1G; (1I) 1D >

(1I) 1C > = 0.3573[f2d2 1G; (1I) 1C > + 0.8567[f2d2 1G; (1I) 1C > + 0.3943[f2d2 1G; (1I) 1C >

(1G) 1C > = 0.3573[f2d2 1G; (1I) 1C > + 0.8567[f2d2 1G; (1I) 1C > + 0.3943[f2d2 1G; (1I) 1C >

(1I) 1B > = 0.3262[f2d2 1G; (1I) 1B > + 0.8567[f2d2 1G; (1I) 1B > + 0.3943[f2d2 1G; (1I) 1B >

(1G) 1B > = 0.3262[f2d2 1G; (1I) 1B > + 0.8567[f2d2 1G; (1I) 1B > + 0.3943[f2d2 1G; (1I) 1B >

(1I) 1A > = 0.3262[f2d2 1G; (1I) 1A > + 0.8567[f2d2 1G; (1I) 1A > + 0.3943[f2d2 1G; (1I) 1A >

(1G) 1A > = 0.3262[f2d2 1G; (1I) 1A > + 0.8567[f2d2 1G; (1I) 1A > + 0.3943[f2d2 1G; (1I) 1A >

(1I) 19 > = 0.3041[f2d2 1G; (1I) 19 > − 0.1099[f2d2 1G; (1I) 19 > + 0.7279[f2d2 1G; (1I) 19 >

(1G) 19 > = 0.3041[f2d2 1G; (1I) 19 > − 0.1099[f2d2 1G; (1I) 19 > + 0.7279[f2d2 1G; (1I) 19 >
Continued.

| (1G) 1I > | 1f2d2 1D; (1G) 1I > | 51 |
| (1G) 1G > | 0.7237 | 2d2 1D; (1D) 1G > | 0.6901 | 2d2 1D; (1G) 1G > | 52 |
| (1D) 1G > | 0.7237 | 2d2 1D; (1D) 1G > | 0.6901 | 2d2 1D; (1G) 1G > | 53 |
| (3H) 5L > | 1f2d2 1F; (3H) 5L > | 54 |
| (3H) 5K > | 1f2d2 3F; (3H) 5K > | 55 |
| (3H) 5I > | 0.8819 | 2d2 3F; (3H) 5I > | 0.4714 | 2d2 3F; (3H) 5I > | 56 |
| (3F) 5I > | 0.8819 | 2d2 3F; (3F) 5I > | 0.4714 | 2d2 3F; (3F) 5I > | 57 |
| (3H) 1I > | -0.4714 | 2d2 3F; (3H) 1I > | 0.8819 | 2d2 3F; (3H) 1I > | 58 |
| (3F) 1I > | 0.4714 | 2d2 3F; (3F) 1I > | -0.8819 | 2d2 3F; (3F) 1I > | 59 |
| (3H) 5H > | 1f2d2 3F; (3H) 5H > | 60 |
| (3F) 5H > | 1f2d2 3F; (3F) 5H > | 61 |
| (3H) 5G > | 0.5283 | 2d2 3F; (3H) 5G > | -0.4866 | 2d2 3F; (3H) 5G > | 62 |
| (3F) 5G > | 0.2762 | 2d2 3F; (3F) 5G > | 0.8819 | 2d2 3F; (3F) 5G > | 63 |
| (3P) 5G > | 0.8591 | 2d2 3F; (3P) 5G > | 0.2808 | 2d2 3F; (3P) 5G > | 64 |
| (3H) 1G > | -0.5118 | 2d2 3F; (3H) 1G > | 0.4714 | 2d2 3F; (3H) 1G > | 65 |
| (3F) 1G > | -0.5118 | 2d2 3F; (3F) 1G > | 0.4714 | 2d2 3F; (3F) 1G > | 66 |
| (3P) 1G > | 0.5118 | 2d2 3F; (3P) 1G > | -0.4714 | 2d2 3F; (3P) 1G > | 67 |
| (3H) 5F > | -0.1592 | 2d2 3F; (3H) 5F > | 0.4864 | 2d2 3F; (3H) 5F > | 68 |
| (3F) 5F > | 0.378 | 2d2 3F; (3F) 5F > | 0.5774 | 2d2 3F; (3F) 5F > | 69 |
| (3P) 5F > | 0.9636 | 2d2 3F; (3P) 5F > | 0.2265 | 2d2 3F; (3P) 5F > | 70 |
| (3H) 1F > | 0.2673 | 2d2 3F; (3H) 1F > | -0.8165 | 2d2 3F; (3H) 1F > | 71 |
| (3F) 1F > | -0.2673 | 2d2 3F; (3F) 1F > | 0.8165 | 2d2 3F; (3F) 1F > | 72 |
| (3P) 1F > | 0.2673 | 2d2 3F; (3P) 1F > | 0.8165 | 2d2 3F; (3P) 1F > | 73 |
| (3H) 5D > | -0.4795 | 2d2 3F; (3H) 5D > | -0.3453 | 2d2 3F; (3H) 5D > | 74 |
| (3F) 5D > | 0.3499 | 2d2 3F; (3F) 5D > | 0.8819 | 2d2 3F; (3F) 5D > | 75 |
| (3P) 5D > | 0.7559 | 2d2 3F; (3P) 5D > | -0.4082 | 2d2 3F; (3P) 5D > | 76 |
| (3H) 3D > | -0.399 | 2d2 3F; (3H) 3D > | -0.543 | 2d2 3F; (3H) 3D > | 77 |
| (1G) 3D > | 0.6712 | 2d2 3F; (1G) 3D > | 0.2808 | 2d2 3F; (1G) 3D > | 78 |
| (1I) 3D > | 0.5575 | 2d2 3F; (1I) 3D > | 0.6022 | 2d2 3F; (1I) 3D > | 79 |
| (3F) 3D > | -0.2912 | 2d2 3F; (3F) 3D > | -0.317 | 2d2 3F; (3F) 3D > | 80 |
| (3P) 3D > | 0.629 | 2d2 3F; (3P) 3D > | -0.2568 | 2d2 3F; (3P) 3D > | 81 |
| (3H) 3D > | 0.6547 | 2d2 3F; (3H) 3D > | 0.4714 | 2d2 3F; (3H) 3D > | 82 |
| (1D) 3D > | 0.6547 | 2d2 3F; (1D) 3D > | 0.4714 | 2d2 3F; (1D) 3D > | 83 |
| (1G) 3P > | 0.346 | 2d2 3F; (1G) 3P > | 0.5099 | 2d2 3F; (1G) 3P > | 84 |
| (3F) 3P > | 0.8321 | 2d2 3F; (3F) 3P > | 0.8321 | 2d2 3F; (3F) 3P > | 85 |
| (1D) 3P > | 0.8133 | 2d2 3F; (1D) 3P > | 0.4714 | 2d2 3F; (1D) 3P > | 86 |
| (1G) 1F > | 0.8452 | 2d2 1D; (1G) 1F > | 0.5345 | 2d2 1D; (1G) 1F > | 87 |
| (1I) 1D > | 0.6831 | 2d2 1D; (1I) 1D > | 0.4646 | 2d2 1D; (1I) 1D > | 88 |
| (3F) 5P > | 1 | 2d2 3F; (3F) 5P > | 95 |
| (3F) 1S > | 1 | 2d2 3F; (3F) 1S > | 96 |
The wavefunctions are given by

$$|a^m_b^n; (S_{\text{o}}, L_{\text{o}})\alpha SL > = \sum_{\alpha' L'S'} (a^{\alpha' b^n}\alpha SL \{|a^\alpha L'S', b^n\}| a^m_b^n; (L'S')SL >$$

Where \((a^{\alpha' b^n}\alpha SL \{|a^\alpha L'S', b^n\}| a^m_b^n; (L'S')SL >)\) is known as coefficient of fractional parentage, \(L', L_{\text{o}}\), \(L\) are orbital angular momenta of parent term, principal parent term and final term of the configurations. Similarly, \(S', S_{\text{o}}, S\) are spin angular momenta of parent term, principal parent term and final term of the configuration.

In this paper all the wavefunctions are given in as shown in equation given below;

$$|{(1S)3P} > = 0.8268| f^2d^2; (1S)3P > + 0.4510| f^2d^2; (3P)3P > + 0.3361| f^2d^2; (1D)3P >$$

All the coefficients of capital letters (e.g. 1S) are multiplicities, all integers after small letters (e.g. f2) are number of electrons. On left hand side the term in bracket is principal parent and the next term is one of the final terms of configuration. The numerical values on right hand side are coefficient of fractional parentage. All the wavefunctions are shown in equation (1) to (106), these wavefunctions are normalized, the wavefunctions of the terms having same values of \(L\) and \(S\) (see table 1) are non-orthogonal, they can be made orthogonal using Gram Schmidt Procedure of orthogonalization. In table 1 final LS terms of the configuration \(4f^25d^2\) of Pr II are given with their frequencies. Table 2 shows that the possible \(J\) values for the configuration lie between \(0 \leq J \leq 10\). The second row of table 2 gives the frequency of occurrence of each of the angular momenta. There are 106 fine levels of Pr II belonging to the configuration mentioned above. Wave functions of these fine levels are given from equation (1) to (106).

As an example, for the calculation of energy of the terms; CFP of the two of the wavefunctions for the terms \(3F\) and \(3H\) have been used to calculate corresponding energies and are compared with the energies given by Ginibre [8]. To calculate coulomb interaction energy following equations have been used [29].

$$E(f^2d^2; 3F) = 0.026F_2(nf; nd) - 0.0815F_2(nf; nd) + 0.127G_1(nf; nd)$$
$$+ 0.1275G_2(nf; nd) - 0.0109G_3(nf; nd)$$

$$E(f^2d^2; 3H) = -0.0699F_2(nf; nd) - 0.0081F_3(nf; nd) + 0.1768G_1(nf; nd)$$
$$+ 0.0891G_3(nf; nd) - 0.0506G_5(nf; nd)$$

To calculate the energy due to spin–orbit interaction following equation is used.

$$d = \left(\frac{3}{2}l(l+1)(2l+1)\right)^{0.5} (-1)^{l+r+j} \left\{\begin{array}{ccc} l & s & j \\ s & l & 1 \end{array}\right\}$$

The total energy calculate with the help of equations (1)–(3) are shown in table 3.

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**Table 3. Term energies of the terms \(^3F\) and \(^3H\).**

| Parent term | Resultant term | \(J\) | Energy | Energy [\(\text{eV}\)] |
|-------------|----------------|------|--------|-------------------|
| 3H          | 3F             | 3    | 25 043.9 | 24 796           |
| 1G          | 3H             | 4    | 25 059.66 | 25 818           |

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**Table 2.** (Continued.)

| \(J\) | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | Total |
|-------|---|---|---|---|---|---|---|---|---|---|----|------|
| \((3P)5D\) > | 1|f^2d^2 3P; (3P)5D > | 97 |
| \((1D)3D\) > | 0.8321|f^2d^2 3P; (3P)3D > + 0.5547|f^2d^2 3P; (1D)3D > | 98 |
| \((3P)3D\) > | 0.8321|f^2d^2 3P; (3P)3D > + 0.5547|f^2d^2 3P; (1D)3D > | 99 |
| \((1D)1S\) > | 1|f^2d^2 1D; (1D)1S > | 100 |
| \((1D)3P\) > | 0.3482|f^2d^2 3P; (1S)3P > - 0.5222|f^2d^2 3P; (3P)3P > + 0.7785|f^2d^2 3P; (1D)3P > | 101 |
| \((3P)3P\) > | 0.3692|f^2d^2 3P; (1S)3P > + 0.8321|f^2d^2 3P; (3P)3P > - 0.4134|f^2d^2 3P; (1D)3P > | 102 |
| \((1S)3P\) > | 0.8018|f^2d^2 3P; (3P)3P > + 0.5976|f^2d^2 3P; (1D)3P > | 103 |
| \((3P)5P\) > | 1|f^2d^2 3P; (3P)5P > | 104 |
| \((3P)1S\) > | 1|f^2d^2 3P; (3P)1S > | 105 |
| \((1S)1S\) > | 1|f^2d^2 1S; (1S)1S > | 106 |
Conclusion

We studied fine structure of Pr II for electronic configuration 4f²5d. It is an even parity configuration. Terms arising from F are used as a parent and are combined with the terms of equivalent electrons d. Coupling of angular momenta is carried out using Russell-Saunders method. Number of terms generated by 4f²5d configuration are 187, most of them are repeated terms with different frequency of occurrence (see table 1). 4f²5d configuration has a total number of 457 fine levels whose angular momenta are given in table 2 and most frequent value for angular momentum is J = 4. Wavefunctions (106 in numbers) are also calculated along with the coefficients of fractional parentage. These wavefunctions could further be used to calculate transition probability, energy, etc. As example calculated energies for the terms ²F and ³H have been shown in table 3.

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