



Ca-I Under Consideration of Foreign Level Configuration Mixing

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Abstract: Weakest Bound Electron Potential Model is a convenient method to determine energies of Rydberg levels. The problem occurs when levels are perturbed due to configuration mixing. In this work, by considering foreign level configuration mixing as perturbation correction, the Rydberg energies transition series: $3p^6 4s 4p^3 P^o_0 \rightarrow 3p^6 4s ns^3 S_1$ ($n=5-50$), $3p^6 4s^2 S_0 \rightarrow 3p^6 4s np^1 P^o_1$ ($n=4-50$), $3p^6 4s 4p^3 P^o_0 \rightarrow 3p^6 4s nd^3 D_1$ ($n=4-50$), $3p^6 4s 4p^3 P^o_1 \rightarrow 3p^6 4s nd^3 D_2$ ($n=4-50$), $3p^6 4s 4p^3 P^o_2 \rightarrow 3p^6 4s nd^3 D_3$ ($n=4-50$) in Ca-I are computed through Weakest Bound Electron Potential Model Theory. The theoretical results are in an excellent agreement with the experimental results listed at NIST.

Keywords: Foreign level configuration, perturbation correction, Rydberg energy levels, weakest bound electron

1. INTRODUCTION

Because of vast applications in the fields of fusion research, plasma physics, physical chemistry and in absorption spectroscopy etc, Rydberg energy levels have been focused at the great extent. The concerned experimental and analytical investigation techniques are developing rapidly. The most renowned techniques are Multi-Channel Quantum Defect Theory, (Leyvraz *et al.*, 2000) (Dai 1995) (Liang *et al.*, 2005). R-matrix and Dirac Hartree Fock Method (Ray 2002), (Blagoev *et al.*, 2001) (Belhout *et al.*, 2007) (Liang *et al.*, 2007). etc. however the theoretical techniques developed has complicated calculation for the many electron systems as fitting of many parameters. Although their results deviate greatly for low excited states rather than high ones. A semi-empirical method called weakest bound electron potential model theory (WBEPMT) (Zheng *et al.*, 2004) was developed in 2004, shows a very close agreement with the experimental values of Rydberg energy levels (Zheng *et al.*, 2003) (Zheng and Sun, 2000) (Tian-Yi and Neng-Wu (2009). (Zheng *et al.*, 2004). (Yildiz 2013) (Zhou *et al.*, 2008) (Ali *et al.*, 2018) (Zheng *et al.*, 2000) (Zhang *et al.*, 2007) (Zhou *et al.*, 2011). (Zheng *et al.*, 2000) (Raza. *et al.*, 2019) (Ahmed *et al.*, 2019). The theory merely based on spectral energy series formed by weakest bound electron (WBE), the many electron system behaves like a hydrogenic atom with the formation of ionic-core and the effective central potential formed due to screening, polarization and penetration effects.

In this communication, five transition series of Rydberg energy states having configurations:

$3p^6 4s 4p^3 P^o_0 \rightarrow 3p^6 4s ns^3 S_1$ ($n=5-50$),
 $3p^6 4s^2 S_0 \rightarrow 3p^6 4s np^1 P^o_1$ ($n=4-50$),
 $3p^6 4s 4p^3 P^o_0 \rightarrow 3p^6 4s nd^3 D_1$ ($n=4-50$),
 $3p^6 4s 4p^3 P^o_1 \rightarrow 3p^6 4s nd^3 D_2$ ($n=4-50$),
 $3p^6 4s 4p^3 P^o_2 \rightarrow 3p^6 4s nd^3 D_3$ ($n=4-50$), in Ca-I are computed by utilizing the WBEPMT with the effects of foreign level configuration mixing called perturbation corrections.

The deviations from experimental results by National Institute of Standards and Technology (NIST) (Kramida, *et al.*, 2018). is not greater than 0.000cm^{-1} , due to high level of computational accuracy occurs by considering the perturbation correction in above mentioned five series, high lying Rydberg energies up to $n=50$ are compute, whose experimental values was not listed at NIST are predicted.

2. MATERIAL AND METHODS

Within the concept's ionization of a free particle the term WBE was presented. WBE in a given atomic or ionic system behave uniquely with respect to all other electrons called NWBE's. in WBE is the most loosely bound electron and can easily get excited or ionized. Since many spectroscopic properties of a system depends upon behaviour of WBE. By knowing the WBE accurately is advantageous. In such considerations many electron systems behave as hydrogenic atom. Therefore, many electron problems can be solved without any complications by assuming it one electron problem within the limits of WBEPMT.

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Let's say in M electron system, M electrons can behave as WBE by consecutive ionization of electrons one after another. The ionized system can be termed as: neutral atom, 1st ionic state, 2nd ionic state, ..., so on till the last Mth electron ionized. The electrons removed in consecutive ionization were termed as 1st, 2nd, 3rd..., Mth WBE. In each ionized system only the one loosely bound electron will be termed as WBE and rest are NWBE's. The nucleus and NWBE's together formed an ionic core, the WBE residing in the effective central potential field caused by ionic-core. Keeping in view the penetration, polarization and screening effects the expression for effective central potential field can be given as (Zheng *et al.*, 2004):

$$V(d) = -\frac{A}{d} + \frac{B}{d^2} \quad \# (1)$$

here,

$$A = Z'$$

and,

$$B = \frac{a(a+1)+2al}{2}$$

Herein equation (1), the first terms on right hand side represent coulombic potential and the 2nd term represent polarization potential as the dipole formed between ion core and WBE, d is the separation distance between WBE's and nucleus, A is the effective nucleus charge (Z') and in B , l is the angular quantum number of WBE's, and 'a' is an unknown parameter, not necessarily an integer.

The Rydberg state energy formula for WBE's is:

$$E = -\frac{1}{2} \left(\frac{Z'}{n'} \right)^2 \quad \# (2)$$

Herein equation (2), n' is the effective principal quantum number. The Z' and n' are unknown values, and are calculated by the transformation between Eigen-values of quantum defect theory (QDT) and WBEPMT, which gives:

$$\frac{Z'}{n'} = \frac{Z_0}{n - \delta_n} \quad \# (3)$$

Herein equation (3), Z_0 is the atomic kernel net charge number and δ_n is the quantum defect in the principal quantum number n . According to this theory the Rydberg energies with or without consideration of perturbation is the sum of ionization limit (E_{lim}) and Rydberg energy (E') of WBE, and is given by (Zheng *et al.*, 2000).

$$E = E_{lim} + E' \quad \# (4)$$

$$E = E_{lim} - \frac{1}{2} \left(\frac{Z_0}{n - \delta_n} \right)^2 \quad \# (5)$$

The quantum defect (δ_n) without considering perturbation correction is computed by Martin's equation is given as: (Martin 1980).

$$\delta_n = a_0 + a_1(n - \delta_0)^{-2} + a_2(n - \delta_0)^{-4} + a_3(n - \delta_0)^{-6} \quad \# (6)$$

In equation (6), δ_0 is the lowest Rydberg state quantum defect of the series, coefficients (a_i 's, $i=0,1,2,3$) in (6) are obtained by the method of least-square fitting of the first few low lying experimental values of the Rydberg energy states of the given series (Shizhong and Qiufeng 2010).. But Rydberg energy states series in Ca-I are perturbed by foreign level configuration mixing of same parity and j ; for treating such Rydberg state series Martin's expression was extended with Langer's (Langer 1930) works. proposed Martin's expression with perturbation correction for computing perturbed Rydberg energy states series (Zheng *et al.*, 2000). The proposed equation is given below:

$$\delta_n = \sum_{i=1}^4 a_i m^{-2(i-1)} + \sum_{j=1}^N \frac{b_j}{m^{-2-\epsilon_j}} \quad \# (7)$$

in which,

$$m = n - \delta_0$$

and,

$$\epsilon_j = \frac{2(E_{lim} - E_{j,per})}{Z_{net}^2} \quad \# (8)$$

In equations (7), N is the number of the foreign perturbing levels and in equations (8), $E_{j,per}$ is the energy of perturbing states.

The regularity of Rydberg energy states and quantum defects of the following five transition series having configurations: $3p^6 4s 4p^3 P^0_{0 \rightarrow 3} p^6 4s ns^3 S_1$ ($n=5-50$),

$$3p^6 4s^2 1S_0 \rightarrow 3p^6 4s np^1 P^0_1 \quad (n=4-50),$$

$$3p^6 4s 4p^3 P^0_{0 \rightarrow 3} p^6 4s nd^3 D_1 \quad (n=4-50),$$

$$3p^6 4s 4p^3 P^0_{1 \rightarrow 3} p^6 4s nd^3 D_2 \quad (n=4-50),$$

$$3p^6 4s 4p^3 P^0_{2 \rightarrow 3} p^6 4s nd^3 D_3 \quad (n=4-50),$$

in Ca-I under the consideration of perturbation correction are studied. To include the effect of foreign level configuration mixing, the quantum defects computed with the extended version of Martin's expression (see equation 7). For the perturbation correction the perturbing states are selected from the data listed at NIST (Kramida, *et al.*, 2018). The perturbing level is the one having same j , parity and lies with in the vicinity of respective Rydberg energy states series, however the effect of perturbing level relies upon the energy of the level. The perturbing states of the Rydberg energies transition series of Ca-I are listed in (Table 1) with their spectral energies in cm^{-1} .

3. RESULT AND DISCUSSION

The coefficient's a_i 's, b_j 's and δ_0 were evaluated by utilizing equations (5), (6) and (7), and listed in Table 2. The Rydberg energies transition series converges under same ionization limit ($E_{limit} = 49305.9240 \text{ cm}^{-1}$) are calculated for all above mentioned five series up to

principal quantum number $n=50$, listed in Table 3-7. All calculated values are in complete agreement with experimental values listed at NIST (Kramida, *et al.*, 2018). as the consideration of perturbation correction. In all cases the deviation is at least 0.000 cm^{-1} .

Table 1: Rydberg Energies Transition Series and Perturbing States with their Energies.

<i>Rydberg Energies Transition Series</i>	<i>Perturbing States</i>	<i>Energy</i> ^[24] [cm^{-1}]
$3p^6 4s 4p^3 P^o_0 \rightarrow 3p^6 4s ns^3 S_1$ ($n=5-50$)	$3p^6 4p 2^3 P_1$	38464.808
	$3p^6 4s 5d^3 D_1$	42743.002
$3p^6 4s 2^1 S_0 \rightarrow 3p^6 4s np^1 P^o_1$ ($n=4-50$)	$3p^6 3d 4p^3 P^o_1$	39335.322
$3p^6 4s 4p^3 P^o_0 \rightarrow 3p^6 4s nd^3 D_1$ ($n=4-50$)	$3p^6 4p 2^3 P_1$	38464.808
$3p^6 4s 4p^3 P^o_1 \rightarrow 3p^6 4s nd^3 D_2$ ($n=4-50$)	$3p^6 4p 2^1 D_2$	40719.847
$3p^6 4s 4p^3 P^o_2 \rightarrow 3p^6 4s nd^3 D_3$ ($n=4-50$)	$3p^6 3d 4p^3 D_3$	38259.124

Rydberg Energies Transition Series and Perturbing States with their Energies.

Rydberg Energies Transition Series: Spectral energy series of bound states of Ca-I, containing perturbing levels

Perturbing States: The foreign levels having same parity and total angular momentum lies within the vicinity of transition series.

Energy ^[24] (cm^{-1}): Energies of Foreign levels used for perturbation correction.

Table 2: The Coefficients Utilized in Equations (6) and (7) of Text.

<i>Coefficients</i>	$3p^6 4s 4p^3 P^o_0 \rightarrow 3p^6 4s ns^3 S_1$	$3p^6 4s 2^1 S_0 \rightarrow 3p^6 4s np^1 P^o_1$	$3p^6 4s 4p^3 P^o_0 \rightarrow 3p^6 4s nd^3 D_1$	$3p^6 4s 4p^3 P^o_1 \rightarrow 3p^6 4s nd^3 D_2$	$3p^6 4s 4p^3 P^o_2 \rightarrow 3p^6 4s nd^3 D_3$
a_0	2.44028	3.12891	1.92573	1.81891	1.78948
a_1	0.38838	-93.08381	-62.37218	-54.30052	-55.49822
a_2	0.22749	1499.44689	1474.35107	1216.81564	1303.70105
a_3	1.34824	-4797.6227	-10654.2330	-7649.20018	-9532.48956
b_1	-0.00001	-0.01170	0.01081	0.00691	0.00750
b_2	0.00001				
δ_0	2.51471	1.93175	0.91866	0.91817	0.91742

The coefficients utilized in equation VI and VII of text.

Rydberg Energies Transition Series: Spectral energy series of bound states of Ca-I, containing perturbing levels

a_1 : Coefficient of Martin's expression.

a_2 : Coefficient of Martin's expression.

a_3 : Coefficient of Martin's expression.

a_4 : Coefficient of Martin's expression.

b_1 : Coefficient of Langer's expression.

b_2 : Coefficient of Langer's expression.

δ_0 : quantum defects of lowest possible state of each transition series.

Table 3: Rydberg Energies Transition Series for $3p^6 4s 4p^3 P^o_0 \rightarrow 3p^6 4s n s^3 S_1$ (n=5-50) in cm^{-1}

Configurations		Quantum Defects		Rydberg Energies (cm^{-1})			$E_{Ul} - E_{cal} (\text{cm}^{-1})$
Lower Level	Upper Level	$\delta_{Ul}^{[24]}$	δ_{Cal}	$E_{Ll}^{[24]}$	$E_{Ul}^{[24]}$	E_{Cal}	
$3p^6 4s 4p^3 P^o_0$	$3p^6 4s 5s^3 S_1$	2.5147	2.5147	15157.901	31539.495	31539.495	0.000
	$3p^6 4s 6s^3 S_1$	2.4750	2.4750		40474.241	40474.241	0.000
	$3p^6 4s 7s^3 S_1$	2.4605	2.4605		43980.767	43980.767	0.000
	$3p^6 4s 8s^3 S_1$	2.4536	2.4536		45738.684	45738.684	0.000
	$3p^6 4s 9s^3 S_1$	2.4498	2.4498		46748.283	46748.283	0.000
	$3p^6 4s 10s^3 S_1$	2.4475	2.4475		47382.048	47382.048	0.000
	$3p^6 4s 15s^3 S_1$		2.4438			48609.878	
	$3p^6 4s 20s^3 S_1$		2.4429			48949.924	
	$3p^6 4s 25s^3 S_1$		2.4426			49090.261	
	$3p^6 4s 30s^3 S_1$		2.4424			49161.423	
	$3p^6 4s 35s^3 S_1$		2.4423			49202.399	
	$3p^6 4s 40s^3 S_1$		2.4423			49228.128	
	$3p^6 4s 45s^3 S_1$		2.4423			49245.335	
	$3p^6 4s 50s^3 S_1$		2.4422			49257.405	

Rydberg Energies Transition Series for all mentioned Transition series in cm^{-1}

Lower Level: Configuration of Lower level of transition.

Upper Level: Configuration of all transition states of upper level.

$\delta_{Ul}^{[24]}$: Quantum defects of known experimental values.

δ_{Cal} : Quantum defects calculated in this work.

$E_{Ll}^{[24]}$: Experimental energy of lower level of transition.

$E_{Ul}^{[24]}$: Experimental energies of all transition states of upper level.

E_{Cal} : Calculated Energies of all transition states of upper levels in this work.

$E_{Ul} - E_{cal} (\text{cm}^{-1})$: Deviation between experimental values and calculated values.

Table 4: Rydberg Energies Transition Series for $3p^6 4s^2 S_0 \rightarrow 3p^6 4s n p^1 P^o_1$ (n=4-50) in cm^{-1}

Configurations		Quantum Defects		Rydberg Energies (cm^{-1})			$E_{Ul} - E_{cal} (\text{cm}^{-1})$
Lower Level	Upper Level	$\delta_{Ul}^{[24]}$	δ_{Cal}	$E_{Ll}^{[24]}$	$E_{Ul}^{[24]}$	E_{Cal}	
$3p^6 4s^2 S_0$	$3p^6 4s 4p^1 P^o_1$	1.9318	1.9318	15157.901	23652.304	23652.304	0.000
	$3p^6 4s 5p^1 P^o_1$	2.0458	2.0458		36731.615	36731.615	0.000
	$3p^6 4s 6p^1 P^o_1$	2.2068	2.2068		41679.008	41679.008	0.000
	$3p^6 4s 7p^1 P^o_1$	1.6822	1.6822		45425.358	45425.358	0.000
	$3p^6 4s 8p^1 P^o_1$	1.7687	1.7687		46479.813	46479.813	0.000
	$3p^6 4s 10p^1 P^o_1$		2.1716			47515.284	
	$3p^6 4s 15p^1 P^o_1$		2.7569			48573.822	
	$3p^6 4s 20p^1 P^o_1$		2.9768			48927.244	
	$3p^6 4s 25p^1 P^o_1$		3.0770			49077.600	
	$3p^6 4s 30p^1 P^o_1$		3.1302			49153.931	
	$3p^6 4s 35p^1 P^o_1$		3.1616			49197.668	
	$3p^6 4s 40p^1 P^o_1$		3.1817			49224.972	
	$3p^6 4s 45p^1 P^o_1$		3.1953			49243.132	
	$3p^6 4s 50p^1 P^o_1$		3.0405			49256.161	

Table5: Rydberg Energies Transition Series for $3p^6 4s 4p^3 P^o_0 \rightarrow 3p^6 4s n d^3 D_1 (n=4-50)$ in cm^{-1}

<i>Configurations</i>		<i>Quantum Defects</i>		<i>Rydberg Energies (cm^{-1})</i>			<i>E_{UI}-E_{cal} (cm^{-1})</i>
Lower Level	Upper Level	$\delta_{UI}^{[24]}$	δ_{Cal}	$E_{LI}^{[24]}$	$E_{UI}^{[24]}$	E_{Cal}	
$3p^6 4s 4p^3 P^o_0$	$3p^6 4s 4d^3 D_1$	0.9187	0.9187	15157.901	37748.197	37748.197	0.000
	$3p^6 4s 5d^3 D_1$	0.9109	0.9109		42743.002	42743.002	0.000
	$3p^6 4s 6d^3 D_1$	0.9227	0.9227		45049.073	45049.073	0.000
	$3p^6 4s 7d^3 D_1$	0.9559	0.9559		46301.973	46301.973	0.000
	$3p^6 4s 8d^3 D_1$	1.0467	1.0467		47036.225	47036.225	0.000
	$3p^6 4s 10d^3 D_1$		1.2425			47875.073	
	$3p^6 4s 15d^3 D_1$		1.5320			48700.933	
	$3p^6 4s 20d^3 D_1$		1.6528			48979.927	
	$3p^6 4s 25d^3 D_1$		1.7112			49103.595	
	$3p^6 4s 30d^3 D_1$		1.7433			49168.485	
	$3p^6 4s 35d^3 D_1$		1.7628			49206.589	
	$3p^6 4s 40d^3 D_1$		1.7754			49230.819	
	$3p^6 4s 45d^3 D_1$		1.7841			49247.166	
	$3p^6 4s 50d^3 D_1$		1.7902			49258.709	

Table 6: Rydberg Energies Transition Series for $3p^6 4s 4p^3 P^o_1 \rightarrow 3p^6 4s n d^3 D_2 (n=4-50)$ in cm^{-1}

<i>Configurations</i>		<i>Quantum Defects</i>		<i>Rydberg Energies (cm^{-1})</i>			<i>E_{UI}-E_{cal} (cm^{-1})</i>
Lower Level	Upper Level	$\delta_{UI}^{[24]}$	δ_{Cal}	$E_{LI}^{[24]}$	$E_{UI}^{[24]}$	E_{Cal}	
$3p^6 4s 4p^3 P^o_1$	$3p^6 4s 4d^3 D_2$	0.9182	0.9182	15157.901	37751.867	37751.867	0.000
	$3p^6 4s 5d^3 D_2$	0.9104	0.9104		42744.716	42744.716	0.000
	$3p^6 4s 6d^3 D_2$	0.9219	0.9219		45050.419	45050.419	0.000
	$3p^6 4s 7d^3 D_2$	0.9542	0.9542		46303.649	46303.649	0.000
	$3p^6 4s 8d^3 D_2$	1.0409	1.0409		47040.007	47040.007	0.000
	$3p^6 4s 10d^3 D_2$		1.2213			47881.968	
	$3p^6 4s 15d^3 D_2$		1.4807			48705.519	
	$3p^6 4s 20d^3 D_2$		1.5873			48982.242	
	$3p^6 4s 25d^3 D_2$		1.6386			49104.850	
	$3p^6 4s 30d^3 D_2$		1.6668			49169.226	
	$3p^6 4s 35d^3 D_2$		1.6838			49207.059	
	$3p^6 4s 40d^3 D_2$		1.6949			49231.135	
	$3p^6 4s 45d^3 D_2$		1.7024			49247.388	
	$3p^6 4s 50d^3 D_2$		1.7078			49258.870	

Table 7: Rydberg Energies Transition Series for $3p^6 4s 4p^3 P^o_2 \rightarrow 3p^6 4s n d^3 D_3$ ($n=4-50$) in cm^{-1} .

Configurations		Quantum Defects		Rydberg Energies (cm^{-1})			$E_{Ul}-E_{cal}(\text{cm}^{-1})$
Lower Level	Upper Level	$\delta_{Ul}^{[24]}$	δ_{cal}	$E_{Ll}^{[24]}$	$E_{Ul}^{[24]}$	E_{cal}	
$3p^6 4s 4p^3 P^o_2$	$3p^6 4s 4d^3 D_3$	0.9174	0.9174	15157.901	37757.449	37757.449	0.000
	$3p^6 4s 5d^3 D_3$	0.9095	0.9095		42747.387	42747.387	0.000
	$3p^6 4s 6d^3 D_3$	0.9207	0.9207		45052.374	45052.374	0.000
	$3p^6 4s 7d^3 D_3$	0.9518	0.9518		46306.059	46306.059	0.000
	$3p^6 4s 8d^3 D_3$	1.0328	1.0328		47045.241	47045.241	0.000
	$3p^6 4s 10d^3 D_3$		1.2066			47886.726	
	$3p^6 4s 15d^3 D_3$		1.4632			48707.074	
	$3p^6 4s 20d^3 D_3$		1.5701			48982.845	
	$3p^6 4s 25d^3 D_3$		1.6218			49105.139	
	$3p^6 4s 30d^3 D_3$		1.6503			49169.385	
	$3p^6 4s 35d^3 D_3$		1.6675			49207.156	
	$3p^6 4s 40d^3 D_3$		1.6787			49231.198	
	$3p^6 4s 45d^3 D_3$		1.6864			49247.431	
	$3p^6 4s 50d^3 D_3$		1.6919			49258.901	

4.**CONCLUSION**

The calculation of energies of Rydberg levels becomes difficult if levels are perturbed and energies of perturbing levels are unknown. In this work within the limits of WBEPMT with the perturbation correction due to foreign level configuration mixing are studied for the following:

$3p^6 4s 4p^3 P^o_0 \rightarrow 3p^6 4s n s^3 S_1$, $3p^6 4s^2 S_0 \rightarrow 3p^6 4s n p^1 P^o_1$,
 $3p^6 4s 4p^3 P^o_0 \rightarrow 3p^6 4s n d^3 D_1$, $3p^6 4s 4p^3 P^o_1 \rightarrow 3p^6 4s n d^3 D_2$,
 $3p^6 4s 4p^3 P^o_2 \rightarrow 3p^6 4s n d^3 D_3$, five low lying Rydberg energies transition series. Total 26 Rydberg energies are computed and found in complete agreement with the experimental values by the NIST [24]. Considering the accuracy of computational method, the predicted values of high lying Rydberg energies up to $n=50$, whose experimental values are not currently available at NIST, are reliable.

In summary we can say that the WBEMPT with perturbation correction is simple and effective method for studying Rydberg energies of transition series in Ca I for both low and high lying principal quantum number. Due to its semi-empirical nature the computation process is accurate and compact. Therefore, the results obtained are in complete agreement with experimental results and deviation is not greater than 0.000 cm^{-1} . So, WBEPMT under consideration of foreign level configuration mixing may be applied widely to study Rydberg energies transition series

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