ARTICLE 17 Excited electron: SPA IV: Silpovgar IV with Piepflui. Excess relativistic: influence in LAN and SPA. **Javier Silvestre** www.eeatom.blogspot.com

ABSTRACT

This is 17th article of 24 dedicated to atomic model based on Victoria equation (Articles index is at end). Relation of Silva de Peral y Alameda (SPA) is studied in [5,7] and refers to excited states and provides linearity between specific energy relationship and LAN of Serelles Secondary Line [2,4] that allows creation of said secondary line obtained from Torrebotana Central Line [1].

[6] and [7] are first and second and this is third and last of three articles that make up a unit. First part of this article concludes Silpovgar study on $n_s \rightarrow ns$ with Mc Flui transform for Silpovgar III and part two of Silpovgar I. Second part is centred on other jumps behaviour that lead to confluence of Silpovgar IV. Third part closes with 5) Other electronic jumps and emphasizes in Silpovgar IV: on the one hand at $X \rightarrow np$ jump location and on the other with Piepflui or Constant spacing. Finally, $1s^2 \rightarrow 1s$ ns (Term=¹S and J=0) brings two main points: Primitive energetic correlation of Silva de Peral y Alameda (SPA PEC) and First application of Relativistic effects.

KEYWORDS

Relation of Silva de Peral y Alameda, SPA relation, Silpovgar IV, Mc Flui transform, Piepflui, FEC, AFEC, PEC, Tete-Vic equation, LAN, Excess relativistic, ER₀, ER_{dR}, Feliz Theory of E_0 , Feliz Representation of E_0

INTRODUCTION

This is third and last of triple article initiated with Relation of Silva de Peral & Alameda II: jump from nss to ns [6] and continued with SPA III: Mc Flui transform for Silpovgar III and Silpovgar IV[7] . Scheme, formulas and figures numbering is unique for three articles giving greater unity sense. Abbreviations Table is at end article. Scheme is as follows:

SPA IV: Silpovgar IV with Piepflui. Excess Relativistic: influence in LAN and SPA 5) Other electronic jumps (Continuation)

C) $n_s(p \text{ or } s) \rightarrow np$ (Term=² P^0 and J=3/2 (or 1/2)) with FEC adapted In general, this point is applied to any $n_s(p^y \text{ or } s^x) \rightarrow n_s(p^{y-1} \text{ or } s^{x-1})$ np P58 $n_s(p^y \text{ or } s^x) \rightarrow n_s(p^{y-1} \text{ or } s^{x-1})$ np jump location in Silpovgar IV P59 Piepflui: Constant spacing for Silpovgar IV

D) $1s^2 \rightarrow 1$ sns (Term=¹S and J=0)

P60 Primitive energetic correlation of Silva de Peral y Alameda (SPA PEC)

6) Relativistic effects: First application made on D) $1s^2 \rightarrow 1$ sns (Term=¹S and $J=0$)

P61 IE Excess Relativistic in SPA PEC

P62 Feliz Theory of E_o vision from electron as moves away. P63 ER^o interatomic behaviour P64 Feliz representation of E_0 vision from electron as moves away.

C) n_s (**p** or s)→np (Term=²**P**⁰ and J=3/2 (or 1/2)) with FEC adapted In general, this point is applied to any $n_s(p^y \text{ or } s^x) \rightarrow n_s(p^{y-1} \text{ or } s^{x-1})$ np

Jumps may need intermediate excited state which is included in FEC conforming adaptation FEC (P57 FEC adapted or AFEC). This intermediate excited state for $n_s p \rightarrow np$ and, in general, for all jump $n_s p^y \rightarrow n_s p^{(y-1)}$ ns is given by (18) and in the case of $n_s s^x \rightarrow n_s x^{(x-1)}$ np by (19):

(18)
$$
n_s p^y \to n_s p^{(y-1)}(n-1)p \to n_s p^{(y-1)}np
$$

(19) $n_s s^x \to n_s x^{(x-1)}(n-1)p \to n_s s^{(x-1)}np$

Initial state \rightarrow intermediate excited state \rightarrow excited state

As indicated in P57 FEC adapted or AFEC, intermediate excited state which is included in FEC conforming adaptation FEC (20). (20) is transformed into (1) when intermediate excited state does not exist.

$$
(20) \text{AFEC} \left[n_s(p^{\text{y}} \text{ or } s^{\text{x}}) \to n_s(p^{\text{y-1}} \text{ or } s^{\text{x-1}}) \text{np} \right] = \frac{-\left(\text{IE} + \text{E}_{k \text{ of } (n-1)p} \right)}{\text{E}_{k \text{ of } np} - \text{E}_{k \text{ of } (n-1)p}}
$$

Silpovgar IV compliance is demonstrated with several isoelectronic series examples with sufficient and accurate data in [7]. These isoelectronic series are in **Table 16.** These examples are represented in **Figure 17** and also converge at the same Piepflui point (FEC=2.75). $2p^*$, $3p^*$ and $4p^*$ are other isoelectronic series with start state in $2p^y$ $3p^y$ and $4p^y$ respectively and have not been individually included. Two np \rightarrow ns jumps are also included because of their relevance in P58. These two isoelectronic series are Al 3p→5s and B 2p→5s and are indicated as Al-5s and B-5s respectively in Figure 17 and Table 16.

	N	$2p^3$ (⁴ S ⁰ 3/2)	[He] $2s^22p^2np(2S^0 1/2)$	N I and O II
			[He] $2s^22p^2np(4P^0 5/2)$	N I and O II
	Ω	$2p^4$ (³ P 2)	[He] $2s^22p^3(^4S^0)$ np (⁵ P 1)	O I and Ne III
			[He] $2s^22p^3(^4S^0)$ np (³ P 0)	O I
Ga		$4p(^{2}P^{0}1/2)$	[Ar] $3d^{10}4s^2np^2P^03/2$	Ga I, Ge II and Kr VI
\mathbf{A}		$3p(^{2}P^{0}1/2)$	[Ne] $3s^2np^2P^03/2$	AI I and Si II
$3p*$	Si	$3p^2$ (³ P 0)	[Ne] $3s^23pnp(^1P_1)$	Si I
	Ar	$3p^6$ (¹ S 0)	[Ne] $3s^23p^5(^2P^03/2)$ np ² [3/2]2	Ar I
Ge		$4p^2$ (³ P 0)	[Ar] $3d^{10}4s^24pnp$ (¹ P 1)	Ge I and Kr V

P58 $\mathbf{n}_s(\mathbf{p}^{\text{y}} \text{ or } \mathbf{s}^{\text{x}}) \rightarrow \mathbf{n}_s(\mathbf{p}^{\text{y-1}} \text{ or } \mathbf{s}^{\text{x-1}})$ np jump location in Silpovgar IV

P58 is $n_s(p^y \text{ or } s^x) \rightarrow n_s(p^{y-1} \text{ or } s^{x-1})$ np jump location in small space of AFEC vs LAN representation and corresponding to np→ns area.

There are two particular relevant details in Figure 17:

* Isoelectronic series are more concentrated in $X \rightarrow 5p$ (Figure 17) than in $X \rightarrow 5s$ (Figure 16). Both axes have been maintained for better comparison between two figures.

* Isoelectronic series concentration zone is located between 3p→5s (Al series) that exerts of centre and two theorists limits equidistant to centre (**Figure 18**):

 $-2p \rightarrow 5s$ (B isoelectronic series)

- Hypothetical limit.

P59 Piepflui: Constant spacing for Silpovgar IV

Piepflui or convergence point in Silpovgar IV representation (AFEC vs. LAN) occurs when LAN=0 and its AFEC value has constant spacing (21). Most of jumps present Silva de Peral y Alameda linearity with AFEC and few exceptions belong to first excited state. n is destiny n or excited state n:

4 1 2n 2 n 4 1 (21)Piepfl ui

P59 Piepflui application examples:

P59.A) $1s^2 \rightarrow$ ns (Term=³S and J=1)

First excited state (1s2s) presents problem to apply (17) since 1p does not exist. Regression, either lineal or polynomial of degree 2 with better $R^2 \rightarrow 1$, tends to 1+1/3 instead of to $1+1/4$ (21). Other jumps comply with P59 Piepflui as is appreciable in **Figure 19** where atoms from He I to Na X are represented.

This intermediate excited state in general case of $n_s s^x \rightarrow n_s x^{(x-1)}$ np is given by (19), but $\sum_{i=1}^{n}$ Term and J should be specified when there is more than one option. In this case,

mechanism is (22). $1s(n-1)p$ (Term=³ P^0 and J=2) has been represented and J can be 0, 1 and 2:

(22) $1s^2 \rightarrow 1s(n-1)p$ (Term=³P⁰ and J=0,1,2) $\rightarrow 1sns$ (Term=³S and J=1)

Slight deviations from P59 Piepflui (21) are reduced when z^s increases (**Figure 20**). This aspect with its possible extrapolation to other electron jumps should be studied with Relation of Riquelme de Gozy curvature developed in next article. Several alternate atoms have been selected for Figure 20: S XV, Sc XX, Ti XXI, Co XXVI, Ga XXX and Kr XXXV.

P59.B) Several jumps

 $\frac{1}{2}$ **Figure 21** has been realized considering mechanisms (14) , (16) , (18) and (19) and formulas (15), (17) and (20). Jump legend indicates: isoelectronic series – destiny n and s or p destiny. For example, "Al-5p" means Aluminium isoelectronic series and 5p \sim destiny (3p→5p). In Figure 21, Piepflui (21) has also been included in regressions calculation for first time. Figure 21 is focused on destiny n equal to 3, 4 or 5.

P59 Piepflui: Constant spacing for Silpovgar IV begins with: "Most of jumps present Silva de Peral y Alameda linearity with AFEC and few exceptions belong to first excited state." First excited state in $n_s p^6 \rightarrow n_s p^5 (n_s+1)s$ is only exception of Figure 21 and therefore are legends: Ne-3s, Ar-4s and Kr-5s and their LAN vs. AFEC points are located following second-order polynomial regression.

Figure 22 is equivalent to Figure 21 but n destiny is the later ones: 6, 7 and 8. Piepflui protagonism is demonstrated in both figures.

D) $1s^2 \rightarrow 1$ sns (Term=¹**S** and **J**=0)

 $1s^2 \rightarrow 1$ sns (Term=³S and J=1) and n_ss \rightarrow ns (Term=²S and J=1/2) has been studied as example fulfilling Relation of Silva de Peral y Alameda (SPA relation) as well as Piepflui point (Figure 19 and 20) [5] and [6]. Another $1s^2 \rightarrow 1$ sns jump remains to be analyzed because there are two destination states (excited states) (**Table 17**). "Destiny state 1" maintains opposite spins as start state and is treated now. "Destiny state 1" is considered as "Primitive Jump" or "First Jump" because is the simplest jump of atom with more than one electron. "Destiny state 1" has particular energetic correlation (EC) as is introduced in [5]. "Primitive Jump" or "First Jump" is governed by P60 Primitive energetic correlation of Silva de Peral y Alameda (SPA PEC).

P60 Primitive energetic correlation of Silva de Peral y Alameda (SPA PEC)

SPA PEC is quotient between 1s ionization energy (E_0) and $1s^2$ ionization energy (IE) (23). SPA PEC is jump energy independent and therefore is outstanding difference with respect to FEC (Fundamental energetic correlation) that is equal to quotient between ionization energy of excitable electron (IE) and excited state energy (E_k) (24).

$$
(23) \text{PEC} = \frac{\text{E}_\text{o}}{\text{IE}}
$$

$$
(24)FEC = \frac{\sqrt{IE'}}{E_k} = \frac{-IE}{E_k}
$$

LAN vs. FEC and PEC for $1s^2 \rightarrow 1s2s$ (Term=¹S and J=0) from He to Kr is represented in **Figure 23**. SPA relation of PEC $(R^2=0.9991)$ is better than $R^2=0.9956$ of FEC. Important difference between both energetic correlations is different sense when z_s increases:

* FEC: \uparrow z_s $\rightarrow \uparrow$ FEC and FEC \rightarrow Fluipoint * PEC: \uparrow z_s \rightarrow LPEC and PEC \rightarrow 1 (IE=E_o)

P61 IE Excess Relativistic in SPA PEC

PEC vs. LAN has slight curvature when Z is high (PEC \rightarrow 1) whose explanation must consider IE which is the most important change between $1s^2 \rightarrow 1s2s$ and another closely studied jump such as $1s^22s \rightarrow 1s^23s$:

> $\langle \text{IE}(1s^2) \rangle \rangle$ /IE(2s)/ for same $z_s \rightarrow 1s2s \text{ ER} \gg 1s^23s \text{ ER}$ and affects to greater extent LAN(1s2s) calculation.

Reversion to linearity is promoted through Excess Relativistic (ER) of $E_{dR}(1s2s)$ which is estimated from 1s ER. 1s ER defined as difference between theoric E_0 (E_{oT}) and experimental E_0 [7] (25):

(25) 1s ER = EoT - E^o = -13.6056899 eV * Z² - E^o

1s ER is obtained from Be to Si, [Be, Si], with $E_0 = [-217.718577, -2673.182]$ and $ER = [0.0275382, 6.4667796]$ and second degree polynomial equation is (26):

(26) 1s ER [Be, Si] = 0,000000932
$$
E_o^2
$$
 + 0,000072416 E_o + 0,000392871
 R^2 = 1,000000

Same operation is performed from Si to Ge with $E_0 = [-2673.182, -14119.429]$ and ER=[6.4667796, 187.202542] and second degree polynomial equation is (27):

(27) 1s ER [Si, Ge] = 0,000000954
$$
E_o^2
$$
 + 0,000231027 E_o + 0,300557746
 R^2 = 1,000000

(25) and (27) are applied for calculation of 1s2s ER, i.e. for first excited state $1s^2 \rightarrow 1s2s$ (Term= 1S and J=0) from He to Kr represented in Figure 23. This 1s2s ER is included in reference destiny energy (EdR) (**Table 18**).

Sc	$-1379,4264$	1,6739	$-1377,7525$
Ti	$-1521,3015$	2,0472	$-1519,2543$
V	$-1670,28$	2,4796	$-1667,8004$
Cr	$-1826,3965$	2,9770	$-1823,4195$
Mn	-1989,6779	3,5459	$-1986, 1320$
Fe	$-2160,1649$	4,1930	$-2155,9719$
Co	-2337,8869	4,9251	$-2332,9618$
Ni	$-2522,8839$	5,7498	$-2517,1341$
Cu	$-2715,1985$	6,6748	$-2708,5237$
Ga	$-3121,7706$	8,8765	$-3112,8941$
Kr	$-4269,834$	16,7069	$-4253, 1271$

PEC vs. LAN of Figure 23 is enlarged in curvature zone with **Figure 24** when curvature increase as PEC decreases is appreciated. In addition, LAN calculated with $E_{dR}(1s2s)$ including ER is represented as LAN*. Conclusion is that $E_{dR}(1s2s)$ including ER corrects LAN curvature and SPA PEC linearity is achieved.

If only Excess Relativistic (ER) of $E_{dR}(1\text{sns})$ effect exists, SPA PEC linearity without considering this effect must be accomplished gradually as n increases because $/E_{dR}/$ decreases and implies ER decreases.

↑n → /EdR/ ↓ → ER ↓ → Effect on LAN ↓ → SPA PEC linearity without 1sns ER

This situation occurs, but more rapidly that predicted by such prior consideration. $1s^2 \rightarrow 1s3s$ (Term=¹S and J=0) without considering E_{dR}(1s3s) ER is already located on SPA PEC linearity marked by LAN* 2s (LAN calculated with $E_{dR}(1s2s)$ including ER) in **Figure 25**. Figure 25 shows $1s^2 \rightarrow 1$ sns for n=[2,5] without ER as LAN ns and LAN calculated with $E_{dR}(1s2s)$ including ER is represented as LAN^* 2s. In addition, $1s^2 \rightarrow 1$ sns with n>3 initiate deviation in reverse direction to that observed with $1s^2 \rightarrow 1s2s$. Conclusion is that there is another effect of inverse sense to E_{dR} ER: Excess Relativistic (ER) of E_0 (1s) is source of this inverse effect because is included in LAN numerator while E_{dR} is in LAN denominator.

Relativistic (ER) of Eo (1s) is introduced with **LAN Feliz solution:**

P62 Feliz Theory of E^o vision from electron as moves away.

Linearity drift resolution in LAN vs. PEC (Figure 25), and in general for SPA relation, is obtained with progressive 1s ER (25) elimination in the vision of said 1s ER (25) by electron as it moves away.

Excess Relativistic (ER) of E_{dR}(1sns) in $1s^2 \rightarrow 1$ sns (Term=¹S and J=0) with n=[3,5] is calculated using (26) because all jumps have $/E_{dR}/2673.182$: Kr 1s3s has high energy with $/E_{dR}/=2113.987$ eV. LAN equation with ER incorporation in E_{dR} and E_0 is given by (28) where ER consideration is indicated with $*$. E_{dR}^* and E_0^* are in (29) and (30). ER_{dR} is Excess Relativistic of reference destiny energy (E_{dR}) in general form to be indicated in (28) since when ER is of concrete jump is represented for example as "1s2s ER" or, more in detail if is not clear, as " $1s2s$ (Term=¹S and J=0) ER". On the other hand, ER_o is Excess Relativistic of 1s ionization energy (E_o) in the vision of said 1s ER (25) by electron as it moves away.

$$
(28) - LAN^* \approx -LAN_R^* = \frac{(-E_o^*)^{1/2} z_s}{(-E_{dR}^*)^{1/2} z_o} - n = \frac{(-E_o - ER_o)^{1/2} z_s}{(-E_{dR} - ER_{dR})^{1/2} z_o} - n
$$

$$
(29) E_{dR}^* = E_{dR} + ER_{dR}
$$

$$
(30) E_o^* = E_o + ER_o
$$

 ER_o value (31) is obtained from (30) and (28):

$$
(31)ER\,circ} = -E\circ -\left[\frac{\left(-\text{LAN}^* + n\right)\left(-\text{Ex}^*\right)^{1/2}Z\circ}{Z\circ}\right]^2
$$

LAN^{*} for $1s^2 \rightarrow 1$ sns (Term=¹S and J=0) is the same that LAN^{*} for $1s^2 \rightarrow 1s2s$ (Figure 24 as LAN^{*} and Figure 25 as LAN^{*} 2s) because PEC is jump energy (E_k) independent. FEC is E_k dependent and thus obtaining LAN^{*} differs. ER_o vs. E_o for $1s^2 \rightarrow 1s$ ns (Term=¹S and J=0) with n=[3,5] is represented in **Figure 25** and shows curves without discontinuities where higher destiny n implies higher ER_0 value. On the one hand, last comment, higher destiny n implies higher ER_0 value, represents first contact with " $P62$ " Feliz Theory of Eo vision from electron as moves away" because verifies progressive 1s ER (25) elimination.

By other hand, $P63$ is intercalated in P62 explanation and develops ER_o interatomic behaviour where, among other conducts, ER_0 vs. E_0 curves must be studied.

P63 ER^o interatomic behaviour

 ER_o , Excess Relativistic of 1s ionization energy (E_o) in the vision of said 1s ER (25) by electron as it moves away, show interatomic trends:

P63.A) ER_0 vs. E_0 has polynomial degree two polynomial regression (Figure 26) according selected n destiny which, considering curve between E^o and 1s ER, ends in P63.B

P63.B) ER_o vs. 1s ER (25) presents linearity as function of selected n destiny (**Figure 27**).

P62 continues with P64: representation of 1s ER (25) elimination in the view from electron as it moves away.

P64 Feliz representation of E^o vision from electron as moves away.

Feliz representation of E_0 vision from electron as moves away is ER_0 vs. $(-E_{dR})^{1/2}$ curve (32). Y-intercept must be equal to 1s ER (25) and therefore said 1s ER must be obtained from extrapolation of experimental data.

$$
(32)ER_\circ \propto \left(-\,E_{\text{dR}}\right)^{\!1/2}
$$

Feliz representation is carried out with Kr $1s^2 \rightarrow 1\$ sns (Term=¹S and J=0 and n=[2,4]) in **Figure 28.** Three jumps are adjusted to grade two polynomial regression (33). Yintercept provided by equation is 295 eV and therefore very close to that expected: 1s ER= ER = E_{oT} - E_o = -13.6056899 eV $*$ 36² - (-17936.208) = 303.23 eV. In addition, $ER_0 \rightarrow 0$ when is Ed_R of 1s4s: $(-Ed_R)^{1/2} = (-4269.834 \text{ eV})^{1/2} = 65.344 \text{ eV}^{1/2}$

$$
(33)ER_{o} = a + b(-E_{dR})^{1/2} + c(-E_{dR})
$$

In fact, inclusion of these two points, $(0, 303.23)$ and $(65.344, 0)$ provide $R^2=0.9999$ in grade two polynomial regression.

For example, Ga and Ti also give values with very good approximation with Y-intercept of 161 and 42 eV against 164 and 41 eV provided by (25).

In next article, corroboration of Feliz Theory of E_0 vision from electron as moves away is done on other jumps as [Ne]3s→[Ne]ns that brings with important differences:

* $/IE$ << /E_o/ implying that ER_{dR} is very small compared to ER_{o} and that difference increases as excitable electron is at higher n. ER_{dR} effect may be negligible especially at low z_s . Therefore, ER_0 effect can be studied individually in some cases.

For example in Na, 1s ionization energy (E_0) is -1648,702 eV and similar to 1s² IE= 1465.121 eV and this has been situation seen in P62, P63 and P64 because jump studied has been: $1s^2 \rightarrow 1$ sns (Term=¹S and J=0). In contrast, for example [He]2s IE=-299,864 eV or especially [Ne]3s IE=-5,13908 eV are much lower. $ER_0 \gg ER_{dR}$ of 3s excited states.

* Electrons with low z_s usually have data at high n and, if also fulfil $\langle IE \rangle \langle E_0 \rangle$, allow to investigate ER₀ individually when $E_{dR}\rightarrow 0$ and consequently X-Axis of Feliz relativistic representation as well: $(E_{dR})^{1/2} \rightarrow 0$.

* ER_0 vs. $(-E_{dR})^{1/2}$ section with medium-high n is approximated to line equation (34) from curve adjusted to grade two polynomial regression (33).

$$
(34)ER_{\circ} \approx a + b\left(-E_{\text{dR}}\right)^{1/2}
$$

* LAN* (28) obtained from SPA relation in present article can also be given by Relation of Riquelme de Gozy [2,3] as seen in following article

Finally, simple study of ER_0 and ER_{dr} effects on LAN is included in annex.

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ANNEX

Energetic changes effect on LAN

LAN has 2 energetic terms (1): Destiny energy of excitable electron that uses reference data [9] (E_{dR}) and born, initial or first electron energy (1s Energy) that is represented by E_{o} .

$$
(1)\text{-}LAN \approx -LAN_\text{R}=\left(\frac{{z_\text{s}}^2{E_\text{o}}}{z_\text{o}^2{E_\text{dR}}}\right)^{1/2}-n=\left(\frac{{z_\text{s}}^2{E_\text{o}}}{z_\text{o}^2{\left(E_\text{K}+I\text{E}\right)}}\right)^{1/2}-n
$$

(1) can be simplified in (2):

$$
(2)\text{-}LAN\approx-LAN_{\scriptscriptstyle R}=\frac{\left(-\,E_{\scriptscriptstyle O}\right)^{\scriptscriptstyle 1/2}z_{\scriptscriptstyle S}}{\left(-\,E_{\scriptscriptstyle dR}\right)^{\scriptscriptstyle 1/2}z_{\scriptscriptstyle O}}-n
$$

Jump energy (E_k) [9] and Ionization energy [8] (IE) provides E_{dR} (3):

$$
(3) E_{dR} = IE + E_k
$$

The energy changes effect on LAN is also applicable on ground state of LAN for $n_s \rightarrow n_s$ jump [3] (4):

$$
(4)\text{-} LAN(\text{P50})=-LAN_\text{ns} \rightarrow \text{ns}=\frac{(-E_\text{o})^{1/2} \, \text{Zs}}{(-IE)^{1/2} \, \text{Zo}} - \text{n}_\text{initial}
$$

Relative Change in percentage is given by (5) where LAN is calculation with (2) and LAN_M is LAN modified. LAN_M also represents actual LAN including Excess Relativistic (ER_o and ER_{dR}) represented by $LAN^*(28)$ and for this reason (5) is thus formulated:

$$
(5)\%RC_M(LAN) = \frac{LAN - LAN_M}{/LAN_M} \bullet 100
$$

(6) implies that energy destiny (E_d) is multiplied by factor F to provide E_{dM}. E_d is generally used and includes possibility of using E_{dR} and E_{dRM} in formulas.

$$
(6)E_{dM}=E_dF
$$

 \uparrow n $\rightarrow \downarrow$ /E_d/ $\rightarrow \downarrow$ /E_d - E_{dM}/ if F=constant (7). That is, Actual change in absolute value decreases as n increases when F=constant. Therefore, if Actual change in absolute value is constant or increases with n is because F also grows with n. This fact is related with two relativistic excess (ER_0 and ER_{dr}).

$$
(7)/E_d - E_{dM}/=E_d\big((1-F)\big)
$$

LAN_M with E_{dM} and LAN with general E_d are in (8) and (9) respectively:

(8) - LAN_M =
$$
\frac{(-E_0)^{1/2}z_s}{(-E_{dM})^{1/2}z_o} - n
$$

$$
(9) - LAN = \frac{(-E_0)^{1/2}z_s}{(-E_d)^{1/2}z_o} - n
$$

 K_{LAN} is inserted into (8) and (9) to reach (11) by applying (5). /LAN_M/ is considered LAN because in most cases LAN is positive.

$$
(10)K_{\rm LAN} \!=\! \frac{(-E_{\rm o})^{1/2}z_{\rm s}}{z_{\rm o}}
$$

$$
(11)\%RC_{\text{M}}(LAN) = \frac{\frac{K_{\text{LAN}}}{(-\text{FE}_{\text{d}})^{1/2}} - n - \frac{K_{\text{LAN}}}{(-\text{Et}_{\text{d}})^{1/2}} + n}{n - \frac{K_{\text{LAN}}}{(-\text{FE}_{\text{d}})^{1/2}}} \bullet 100
$$

Sum of terms allows transition from (11) to (12):

$$
(12)\%RC_{\text{M}}(LAN) = \frac{\frac{K_{\text{LAN}} - F^{1/2}K_{\text{LAN}}}{(-FE_{\text{d}})^{1/2}}}{\frac{-K_{\text{LAN}} + n(-FE_{\text{d}})^{1/2}}{(-FE_{\text{d}})^{1/2}}} \bullet 100
$$

(13) is (12) with both denominators simplified:

$$
(13)\%RC_{M}(LAN) = \frac{K_{LAN} - F^{1/2}K_{LAN}}{-K_{LAN} + n(-FE_{d})^{1/2}} \bullet 100
$$

(14) is (13) divided numerator and denominator by K_{LAN} :

$$
(14)\%RC_M(LAN) = \frac{1 - F^{1/2}}{-1 + \frac{n(-FE_d)^{1/2}}{K_{LAN}}} \bullet 100
$$

(15) is obtained from (9) and (10). (15) use causes (16) to be achieved from (14):

$$
(15)n - LAN = \frac{K_{\text{LAN}}}{(-E_{\text{d}})^{1/2}}
$$

$$
(16)\%RC_M(LAN) = \frac{1 - F^{1/2}}{-1 + \frac{nF^{1/2}}{n - LAN}} \bullet 100
$$

 (17) is (16), but considering LAN_M instead of LAN.

$$
(17)\%RC_M(LAN) = \frac{1 - F^{1/2}}{n}
$$
 \bullet 100

$$
1 + \frac{n}{n - LAN_M}
$$

Three interesting situations are:

a) %RC_M(LAN)→100% when n→∞ (18). (16) with n→∞ is transformed into (18) and %RCM(LAN)→100% because infinite terms are simplified each other and cause numerator and denominator to be identical:

$$
(18)\%RC_{M}(LAN)_{n\to\infty} = \frac{1-F^{1/2}}{-1+\frac{\infty F^{1/2}}{\infty}} \bullet 100 = -100\%
$$

b) %RC_M(LAN) \rightarrow 100% when LAN \rightarrow 0 (19). (16) with LAN \rightarrow 0 is transformed into (19) and % $RC_M(LAN) \rightarrow 100\%$ because LAN is negligible compared to n value and consequently situation is identical to previous one: numerator and denominator are identical:

$$
(19)\%RC_{M}(LAN)_{LAN\rightarrow 0} = \frac{1 - F^{1/2}}{-1 + \frac{nF^{1/2}}{n}} \bullet 100 = -100\%
$$

(18) and (19) occur because (5) is changed to (5.B.) when $n \rightarrow \infty$ or LAN $\rightarrow 0$:

$$
(5.B.)\%RC_{M}(LAN)_{LAN\rightarrow 0} = \%RC_{M}(LAN)_{n\rightarrow \infty} = \frac{LAN-LAN_{M}}{/LAN_{M}} \bullet 100 = \frac{-LAN_{M}}{/LAN_{M}} \bullet 100 = -100\%
$$

 -100% has been indicated because LAN (and LAN_M) is mostly positive.

100

is transformed into (18) and

fied each other and cause
 $= -100\%$

AN- \rightarrow 0 is transformed into

e compared to n value and

erator and denominator are
 $= -100\%$
 $\rightarrow \infty$ or LAN- \rightarrow 0:
 $= -100\%$
 $\rightarrow \infty$ or LAN- \rightarrow Therefore, both higher n and lower LAN imply an increase in deviation between both LAN. Lower LAN has been observed with z_s is increased [2,7]. All this leads to work with data from n↑ and LAN↓ (or $z_s \uparrow$) is less accurate in SPA or RG relations. In addition, is necessary to add own experimental difficulties that present LAN value when $n \uparrow$ and $z_s \uparrow$.

c) %RC_M(LAN)→±∞

This discontinuity is produced when (16) denominator is cancelled and is called discontinuity condition (33). n discontinuity condition (34) is obtained from (33) and is positive with physical sense if $0 < F < 1$ since LAN is positive. This discontinuity causes that % $RC_M(LAN)$ vs. n curve to be different with $0 < F < 1$ or $F > 1$.

(33)Discon tinuity condition =
$$
-1 + \frac{nF^{1/2}}{n - LAN} = 0
$$

(34)n discontinu ity condition = $\frac{LAN}{1 - F^{1/2}}$

a) and b) interesting situations discussed and high LAN sensibility to energetic variations can be verified with **Figure 29**. Figure 29 is $% RC_M(LAN)$ vs. $log(n)$ curve with (16). X-axis is $log(n)$ is for better visualization up to high n. LAN plain [2] is considered approximately constant. LAN value of third n destiny is selected so that approximation is more correct for high n destiny. These LAN value of third n destiny are as follows for indicated samples:

Figure 29 shows that both higher n and lower LAN imply an increase in deviation between both LAN (point a) and b) commented previously).

High sensitivity is also checked. (E_d) is multiplied by factor F to provide E_{dM} (6) and F selected is 1.001, i.e. variation of 0.1 %. LAN sensibility to energetic variations is corroborated because variations are much higher that 0.1 % (% $RC_M(LAN)$)>0.1%)

Even jumps with higher LAN (Li 2s→ns and Na 3s→ns) and lower n show %RC_M(LAN)>0.1%. (**Figure 30**). Figure 30 is %RC_M(LAN) vs. n curve with (16). Xaxis is n and not $log(n)$ to focus study at low n.

(20) and (6) are equalized as indicated in (21) if E_d deviation is x (20)

$$
(20)E_{dM} = E_d + x
$$

$$
(21)E_dF = E_d + x
$$

F (22) is obtained from (21) as x function and this F expression is included in (16) to arrive at (23):

$$
(22)F = \frac{E_d + x}{E_d}
$$

$$
(23)\%RC_{M}(LAN) = \frac{1 - \left(\frac{E_{d} + x}{E_{d}}\right)^{1/2}}{n\left(\frac{E_{d} + x}{E_{d}}\right)^{1/2}} \bullet 100
$$

$$
-1 + \frac{1}{n - LAN}
$$

(23) application with x=0.001 eV is performed on same jumps of Figures 29 and 30. $x=0.001$ eV because provides similar deviation as with $F=1,001$ for first jump shown. **Figure 31** represents % $RC_M(LAN)$ vs. $Log(n)$ curve with $x=0,001$ eV. Main conclusion is that %RC_M(LAN) increases faster with $x=0,001$ than with $F=1,001$ because E_d is decreasing and $x=constant=0.001$ eV is summed, and not multiplied as F, to E_d. x=constant provides growing F as n increases (22):

$$
n\uparrow \rightarrow \downarrow/E_d \rightarrow \uparrow F \text{ (if x=constant)} \rightarrow \uparrow \text{/%RCM(LAN)}
$$

%RC_M(LAN) has more dramatic variations if situation is reverse: F<1 or $x\le 0$. Discontinuity pointed out in c) % $RC_M(LAN) \rightarrow \pm \infty$ provokes said variability increase. n discontinuity condition applied to F (34) is extended to x (35).

(35)n discountinu ity condition
$$
=
$$
 $\frac{\text{LAN}}{1 - \text{F}^{1/2}} = \frac{\text{LAN}}{1 - \left(\frac{\text{E}_d + x}{\text{E}_d}\right)^2}$

 E_d (36) is obtained from (15) and inserted into (35) to provide (37):

$$
(36)E_{d} = -\left(\frac{K_{LAN}}{n - LAN}\right)^{2}
$$
\n
$$
(37)n \text{ discontinu ity condition } = \frac{LAN}{1 - F^{1/2}} = \frac{LAN}{1 - \left(\frac{K_{LAN}}{n - LAN}\right)^{2} + x}\left(\frac{-(\frac{K_{LAN}}{n - LAN})^{2}}{-(\frac{K_{LAN}}{n - LAN})^{2}}\right)^{2}}
$$

(37) calculation for jumps with x can be obtained after calculating resulting third degree equation.

Jumps with elevated LAN may appear to have lower $% RC_M(LAN)$ considering what is seen in Figure 29 and 31, but one element of capital importance is missing: increasing LAN (for same jump and z_s) requires raising n_s and this implies increasing z_0 (i.e. atomic number) and its associated ER_0 (Excess Relativistic of 1s ionization energy (E_0) in the vision of said 1s ER).

Consequently, Cs I 6s \rightarrow ns with respect to Na I 3s \rightarrow ns has two opposite effects:

Positive: \uparrow LAN $\rightarrow \downarrow\%$ RCM(LAN) Negative: \uparrow Z (or z_o) $\rightarrow \uparrow$ /E_o/ $\rightarrow \uparrow$ ER_o $\rightarrow \uparrow$ %RCM(LAN)

Negative effect wins and, for example in this Cs I 6s→ns, Relation of Riquelme de Gozy without ER_0 considerations has much greater curvature than Na I 3s \rightarrow ns.

G is E_0 deviation factor (24) in analogy to F with E_d (6). (24) implies that 1s ionization energy (E_0) is multiplied by factor G to provide E_{oM} . (16) remains as (25) with E_{oM} inclusion:

 $(24)E_y - E$ ^G

$$
(25)\%RC_{M}(LAN) = \frac{1 - \left(\frac{F}{G}\right)^{1/2}}{n\left(\frac{F}{G}\right)^{1/2}} \cdot 100
$$

$$
-1 + \frac{n\left(\frac{F}{G}\right)^{1/2}}{n-LAN}
$$

(8.B) expresses LAN_M with modification in both energies. % $RC_M(LAN)=0$ when F=G because LAN_M=LAN and can also be seen as (25) is changed to (26)

$$
(8.B) - LAN_{M} = \frac{(-E_{cM})^{1/2}Z}{(-E_{dM})^{1/2}Z_{c}} - n = \frac{(-E_{c}C)^{1/2}Z}{(-E_{d}C)^{1/2}Z_{c}} - n = \frac{(-E_{c} - y)^{1/2}Z}{(-E_{d}C - x)^{1/2}Z_{c}} - n
$$

\n
$$
(26)\%RC_{M}(LAN)_{F=G} = \frac{1-1}{-1+\frac{n}{n-LAN}} \bullet 100 = \frac{0}{-1+\frac{n}{n-LAN}} \bullet 100 = 0
$$

\n
$$
(27)(28)(29) \text{ play the same role as F and x } (20)(21)(22):
$$

\n
$$
(27)E_{M} = E_{v} + y
$$

\n
$$
(28)E_{v}G = E_{v} + y
$$

\n
$$
(29)G = \frac{E_{v} + y}{E_{o}}
$$

\n
$$
(29)G = \frac{E_{v} + y}{E_{o}}
$$

\n
$$
(30) - LAN^{*} \approx -LAN_{R}^{*} = \frac{(-E_{v})^{1/2}Z_{c}}{(-E_{d}C_{c}^{*})^{1/2}Z_{c}} - n = \frac{(-E_{o} - ER_{u})^{1/2}Z_{c}}{(-E_{d}C_{c} - ER_{u})^{1/2}Z_{c}} - n
$$

\n
$$
(31) x = ER_{dR}
$$

\n
$$
(32) y = ER_{o}
$$

\n25

G and y (27)(28)(29) play the same role as F and x (20)(21)(22):

$$
(27)EoM = Eo + y
$$

$$
(28)EoG = Eo + y
$$

$$
(29)G = \frac{Eo + y}{Eo}
$$

LAN^{*} (30) (seen as (28) in article) is specific case in which relativistic effects on LAN are calculated and where x is (31) and y is (32):

(30) - LAN^{*}
$$
\approx
$$
 -LAN^{*} $=$ $\frac{(-E_{o}^{*})^{1/2}z_{s}}{(-E_{dR}^{*})^{1/2}z_{o}} - n = \frac{(-E_{o} - ER_{o})^{1/2}z_{s}}{(-E_{dR} - ER_{dR})^{1/2}z_{o}} - n$
(31) $x = ER_{dR}$
(32) $y = ER_{o}$

