Screening Constant by Unit Nuclear Charge Calculations of Resonance Energies of the $3(K, T, A)_n^{1,3}L^\pi$ Rydberg Series of He-Like Ions

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To cite this article:
Jean Kouhissoré Badiane, Abdourahmane Diallo, Mamadou Dioulo Ba, Momar Tall Gning, Malick Sow, Ibrahima Sakho. Screening Constant by Unit Nuclear Charge Calculations of Resonance Energies of the $3(K, T, A)_n^{1,3}L^\pi$ Rydberg Series of He-Like Ions. International Journal of Applied Mathematics and Theoretical Physics. Vol. 4, No. 2, 2018, pp. 55-60. doi: 10.11648/j.ijamtp.20180402.14

1. Introduction

Helium-like systems are very rich in structures attributed to doubly excited states with mixed configurations. Studies of autoionizing states in the helium isoelectronic sequence are very useful prototypes for the analysis of “many-particles” investigations. As the independent particles model is unappropriated for interpreting doubly excited states (DES) of He-like systems, most atomic spectra are treated on the classification scheme with the set of correlation quantum numbers $K, T$ and $A$. For a given state of He-like systems, the classification scheme is labelled as $N(K, T, A)^{2S+1}L^\pi$ [1].

For the DES converging to the $N = 2$ hydrogenic threshold, the Screening constant by unit nuclear charge (SCUNC) has been used previously [2, 3] to report accurate results for He-like systems. Using the complex-coordinate rotation (CCR) method, Chung and Lin [4] studied over 540 doubly excited states of Li$^+$ resonances below the $N = 2$ and $N = 3$ thresholds and tabulated relativistic resonances parameters by grouping the DES into Rydberg series labelled in the $(K, T, A)$ scheme classification. Using the Feshbach formalism, Bachau et al., [5] reported a complete set of data belonging to the lowest resonances of $^{1}S^0$, $^{1}P^0$, $^{3}P^0$, $^{1}P^2$, and $^{3}P^2$ symmetries of He-like doubly excited states lying between the $N = 2$ and $N = 3$ thresholds with $Z = 2-10$. But, energy positions are missing for $Z > 10$ and in the NIST database, no data is quoted for the Rydberg series of the helium-isoelectronic series converging to the $N \geq 3$ hydrogenic thresholds. In addition, it is also challenging to succeed on interpreting quantitatively the physical meaning of the $K$ correlation quantum number. In fact, if $T$ is roughly speaking the projection of $L$ onto the interelectronic axis and describes then the orientations between the orbitals of the two electrons, $K$ is related to the cosinus of the angle between the position vectors of the two electrons. Physically, the larger the value of $K$, the value of $-\cos \theta_2$ is closer to unity. In addition for states with positive $K$, $r_{12}$ increases and while for states with negative $K$, $r_{12}$ decreases while $\frac{1}{N^{1/2}}$ increases as explained recently [6].
of new quantum models for interpreting atomic spectra must first be appropriated in the well description of electron-electron correlation and relativistic effects in two electron systems. So a complete description of all the Rydberg series belonging to the He-like systems is necessary.

The goal of the present study is to extend recent calculations of Sakho [6] on the \( ^{1+}P_n \) \( ^{1D_n}, \ (0,2,+)_n \) \( ^{1D_n}, \ (1,1,+)_n \) \( ^{1D_n}, \ (1,1,+)_n \) \( ^{1P_n}, \ (1,1,+)_n \) \( ^{1P_n}, \ (1,1,+)_n \) \( ^{1P_n}, \ (1,1,+)_n \) \( ^{1F_n}, \ (2,0,+)_n \) \( ^{1G_n}, \ (1,1,+)_n \) \( ^{1D_n}, \ (1,1,+)_n \) \( ^{1F_n}, \ (2,0,+)_n \) \( ^{1F_n} \) Rydberg series of Helium-like ions \( Z = 3-40 \) applying the Screening constant by unit nuclear charge (SCUNC) method. Quantitative interpretation of the \( - \) angular correlation quantum number is also aimed in this work. In section 2 presents the theoretical procedure adopted in this work. The results obtained are discussed in section 3.

2. Theory

2.1. Brief Description of the SCUNC Formalism

In the framework of Screening constant by unit Nuclear charge formalism, total energy of \( (N', n\ell) ^{2S+1}L^\pi \) excited states are expressed in the form

\[
E(N'n\ell' ; ^{2S+1}L^\pi ; Z) = - Z^2 \left( \frac{1}{N^2} + \frac{1}{n^2} \left[ 1 - \beta \left( N'n\ell' ; ^{2S+1}L^\pi ; Z \right) \right] \right) \text{Ryd} \tag{1}
\]

In this equation, the principal quantum numbers \( N \) and \( n \), are respectively for the inner and the outer electron of He-isoelectronic series. In this equation, the \( \beta \)-parameters are screening constant by unit nuclear charge expanded in inverse powers of \( Z \) and given by

\[
\beta \left( N'n\ell' ; ^{2S+1}L^\pi ; Z \right) = \sum_{k=1}^{q} f_k \left( \frac{1}{Z} \right)^k \tag{2}
\]

where \( f_k = f_k \left( N'n\ell' ; ^{2S+1}L^\pi \right) \) are parameters to be evaluated.

With respect to the new classification scheme, equation (1) takes the form \[2, 3]\]

\[
E_{n} (K, T, A) ^{2S+1}L^\pi = - Z^2 \left( \frac{1}{N^2} + \frac{1}{n^2} \left[ 1 - \beta \left( N'n\ell' ; ^{2S+1}L^\pi ; Z \right) \right] \right) \text{Ryd} \tag{3}
\]

Using equation (2), we get from (3)

\[
E_{n} (K, T, A) ^{2S+1}L^\pi = - Z^2 \left( \frac{1}{N^2} + \frac{1}{n^2} \left[ 1 - \sum_{k=1}^{q} f_k \left( K, T, A \right) ^{2S+1}L^\pi \left( \frac{1}{Z} \right)^k \right] \right) \text{Ryd} \tag{4}
\]

2.2. Expressions of the Resonance Energies

For all the Rydberg series investigated in the present work and lying to the \( N' = 3 \) hydrogenic threshold, total energy is expressed as follows using Eq. (4)

\[
E_n = - Z^2 \left[ \frac{1}{9} + \frac{1}{n^2} \left( 1 - f_1 \left[ K, T, A \right] ^{2S+1}L^\pi \right) \frac{Z}{(n-1)} \right] - \frac{f_2 \left[ K, T, A \right] ^{2S+1}L^\pi}{Z} + \frac{f_1 \left[ K, T, A \right] ^{2S+1}L^\pi \times (Z - Z_0)}{Z^3 (n + 3)} \right) \text{Ryd} . \tag{5}
\]

The \( f_1 \left[ K, T, A \right] ^{2S+1}L^\pi \)-screening constants in Eq. (5) are evaluated from accurate relativistic data of Chung and Lin [4] on Li\(^{+}\). To take into account the effect of the nucleus volume with increasing \( Z \), a tiny correction of type we have introduced in Eq. (5)

\[
f_1 \left[ K, T, A \right] ^{2S+1}L^\pi \times (Z - Z_0) \]

\[
Z^3 (n + 3)
\]

The \( f_1 \left[ K, T, A \right] ^{2S+1}L^\pi \)-screening constants in Eq. (5) are evaluated from accurate relativistic data of Chung and Lin [4] on Li\(^{+}\) \( (Z_0 = 3) \). If we denote by \( E \left[ K, T, A \right] ^{2S+1}L^\pi \) the energy positions measured with respect to the ground state \( E_0 \) of Li\(^{+}\), total energy (5) is given by

\[
E_n = E \left[ K, T, A \right] ^{2S+1}L^\pi - E_0 . \tag{6}
\]

For Li\(^{+}\), \( E_0 = - 198.0977 \) eV and the reduced Rydberg is equal to 13.604635 eV [4].

The present study is limited to the Rydberg series starting with the lowest \( n = 3 \) resonance.

3. Results and Discussion

The results obtained in this work are listed in Tables 1-6.
The resonances are ordered so that total energy decreases along the series. For example, the total energies of the $j(2,0)^{3}\text{P}^0$, $j(2,0)^{3}\text{F}^0$, and $j(2,0)^{3}\text{G}^0$ states of helium-like ions are seen to be very good. It should be underlined the lack of precision in the FF computations for the $j(2,0)^{3}\text{F}^0$ and $j(2,1)^{3}\text{D}^0$ levels mentioned with the same value of total energies at 10.4800 a. u. For these levels, the present SCUNC predictions are equal to 10.4871 a. u. for the $j(2,0)^{3}\text{F}^0$ level and 10.4726 a. u. for the $j(2,1)^{3}\text{D}^0$ state. The SCUNC data at 10.4726 a. u. may then be preferable.

Table 1. Total energy $\epsilon$-$E$, in a. u. for the $j(2,0)^{3}\text{D}^0$, $j(2,1)^{3}\text{F}^0$, $j(2,0)^{3}\text{F}^0$, and $j(2,1)^{3}\text{D}^0$ states of helium-like ions (Z = 3-12). The present screening constant by unit nuclear charge (SCUNC) calculations are compared with the Feshbach formalism (FF) results of Bachau et al., [5].

| Z     | $j(2,0)^{3}\text{D}^0$ | FF       | SCUNC    | FF       | SCUNC    | FF       | SCUNC    | FF       | SCUNC    | FF       | SCUNC    | FF       | SCUNC    | FF       | SCUNC    | FF       | SCUNC    | FF       | SCUNC    | FF       | SCUNC    | FF       | SCUNC    | FF       |
|-------|------------------------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|
| 3     | 0.8422                 | 0.8447   | 0.6686   | 0.6697   | 0.8313   | 0.8331   | 0.6611   | 0.6618   | 0.6618   | 0.6618   | 0.6618   | 0.6618   | 0.6618   | 0.6618   | 0.6618   | 0.6618   |
| 4     | 1.5663                 | 1.5670   | 1.2356   | 1.2360   | 1.5512   | 1.5510   | 1.2250   | 1.2250   | 1.2250   | 1.2250   | 1.2250   | 1.2250   | 1.2250   | 1.2250   | 1.2250   | 1.2250   |
| 5     | 2.5112                 | 2.5110   | 1.9757   | 1.9760   | 2.4919   | 2.4919   | 1.9619   | 1.9620   | 1.9620   | 1.9620   | 1.9620   | 1.9620   | 1.9620   | 1.9620   | 1.9620   | 1.9620   |
| 6     | 3.6776                 | 3.6770   | 2.8891   | 2.8890   | 3.6540   | 3.6530   | 2.8720   | 2.8720   | 2.8720   | 2.8720   | 2.8720   | 2.8720   | 2.8720   | 2.8720   | 2.8720   | 2.8720   |
| 7     | 5.0658                 | 5.0650   | 3.9758   | 3.9750   | 5.0378   | 5.0370   | 3.9555   | 3.9560   | 3.9560   | 3.9560   | 3.9560   | 3.9560   | 3.9560   | 3.9560   | 3.9560   | 3.9560   |
| 8     | 6.6758                 | 6.6750   | 5.2361   | 5.2360   | 6.6436   | 6.6440   | 5.2125   | 5.2140   | 5.2140   | 5.2140   | 5.2140   | 5.2140   | 5.2140   | 5.2140   | 5.2140   | 5.2140   |
| 9     | 8.5079                 | 8.5080   | 6.6698   | 6.6700   | 8.4713   | 8.4720   | 6.6430   | 6.6450   | 6.6450   | 6.6450   | 6.6450   | 6.6450   | 6.6450   | 6.6450   | 6.6450   | 6.6450   |
| 10    | 10.5621                | 10.5600  | 8.2771   | 8.2770   | 10.5211  | 10.5220  | 8.2470   | 8.2500   | 8.2500   | 8.2500   | 8.2500   | 8.2500   | 8.2500   | 8.2500   | 8.2500   | 8.2500   |
| 11    | 12.8384                | 12.0579  | 10.0759  | 10.0770  | 12.7930  | 10.0246  | 11.9758  | 12.0579  | 10.0770  | 10.0246  | 11.9758  | 12.0579  | 10.0770  | 10.0246  | 11.9758  | 12.0579  |
| 12    | 15.3368                | 12.0123  | 15.2870  | 11.9758  | 15.2870  | 11.9758  | 15.2870  | 11.9758  | 15.2870  | 11.9758  | 15.2870  | 11.9758  | 15.2870  | 11.9758  | 15.2870  | 11.9758  |

Table 2 compares the present SCUNC charge results for excited $j(0, 2)^{3}\text{D}^0$, $j(0, 2)^{3}\text{F}^0$, and $j(0, 2)^{3}\text{G}^0$ Rydberg series of helium-like ions (Z = 3-12). Here again, the agreements between the calculations are very good up to Z = 10.

Table 2. Total energy $\epsilon$-$E$, in a. u. for the $j(0, 2)^{3}\text{D}^0$, $j(0, 2)^{3}\text{F}^0$, and $j(0, 2)^{3}\text{G}^0$ states of helium-like ions with the FF predictions of Bachau et al., [5]. Here again, the agreements between the calculations are very good up to Z = 10.
The very good agreements between the SCUNC and the FF [5] calculations are also obtained comparing the results quoted in Table 3 and 4 respectively for the $\tilde{s}(1,1)_{n}^{1}p^0$, $\tilde{s}(-1,1)_{n}^{3}p^0$ and $\tilde{s}(1,1)_{n}^{3}D^+$ (n = 3-4) states of He-like ions (Z = 3-10).

The result of table 5 presents calculations of excitation energies for doubly $^{1,3}L^2$ (L = P, D, F, G) and $^{1,3}L^4$ (L = D, F) excited states of He-like (Z = 4-10) systems. Energies are calculated with respect to the ground state of the corresponding system. Comparison is done with some literature data such as those from Density functional theory (DFT) of Roy et al., [11], Complex rotation method (CCR) of Ho and Bathan [12], and time-dependent variation perturbation (TDVP) of Ray and Mukherjee [13] and those from Multiconfiguration (MC) of Lipsky et al., [14]. It should be underlined that, in the DFT and TDVP models, the doubly excited states are labeled in the $\tilde{n}n$ $^{2s+1}L^2$ notation disregarding the appropriated $\tilde{s}(K, T, A)_n^{2s+1}L^2$ classification scheme. Overall good agreement are obtained between the calculations.

| n | $\tilde{s}(1,1)_{n}^{1}p^0$ | $\tilde{s}(-1,1)_{n}^{3}p^0$ | $\tilde{s}(1,1)_{n}^{3}D^+$ |
|---|---|---|---|
| Z | SCUNC | FF | SCUNC | FF | SCUNC | FF |
| 3 | 0.7720 | 0.7710 | 0.6425 | 0.7557 | 0.7560 | 0.6250 |
| 4 | 1.4640 | 1.4580 | 1.1969 | 1.4418 | 1.4430 | 1.1717 |
| 5 | 2.3777 | 2.3660 | 1.9247 | 2.3490 | 2.3510 | 1.8915 |
| 6 | 3.5133 | 3.4960 | 2.8259 | 3.7778 | 3.4820 | 2.7846 |
| 7 | 4.8709 | 4.8480 | 3.9060 | 4.8285 | 4.8360 | 3.8511 |
| 8 | 6.4505 | 6.4220 | 5.1490 | 6.4012 | 6.4110 | 5.0912 |
| 9 | 8.2523 | 8.2190 | 6.5708 | 8.1958 | 8.2090 | 6.5048 |
| 10 | 10.2763 | 10.2400 | 8.1662 | 10.2162 | 10.2300 | 8.0919 |
| 11 | 12.5294 | 9.9352 | 12.4515 | 9.8526 |
| 12 | 14.9907 | 11.8778 | 14.9125 | 11.7868 |

| n | $\tilde{s}(1,1)_{n}^{1}D^+$ | $\tilde{s}(1,1)_{n}^{3}D^+$ |
|---|---|---|
| Z | SCUNC | FF | SCUNC | FF |
| 3 | 0.8131 | 0.8131 | 0.6530 | 0.6533 |
| 4 | 1.5251 | 1.5240 | 1.2131 | 1.2120 |
| 5 | 2.4580 | 2.4550 | 1.9463 | 1.9440 |
| 6 | 3.6125 | 3.6090 | 2.8528 | 2.8500 |
| 7 | 4.9887 | 4.9850 | 3.9327 | 3.9290 |
| 8 | 6.5868 | 6.5830 | 5.1861 | 5.1810 |
| 9 | 8.4069 | 8.4040 | 6.6129 | 6.6060 |
| 10 | 10.4491 | 10.4500 | 8.2133 | 8.2050 |
| 11 | 12.7134 | 9.9873 |
| 12 | 15.1998 | 11.9348 |
positive on the opposite sides of the nucleus, as a result the TDVP, time-dependent variation perturbation, Ray and Mukherjee [13].

CCR, complex rotation method, Ho and Bathia [12].

DFT, Density functional theory, Roy et al., [11].

given by (in a.u) [6]

-SCUNC, Screening constant by unit nuclear charge, present work

FF, Feshbach formalism, Bachau et al., [5].

DFT, Density functional theory, Roy et al., [11].

CCR, complex rotation method, Ho and Bathia [12].

TDVP, time-dependent variation perturbation, Ray and Mukherjee [13].

MC, Multiconfiguration, Lipsky et al. [14].

On the other hand, according to the physical meaning of the K correlation angular quantum number, for states with positive K, the two electrons tend to stay on the opposite sides of the nucleus while in states with negative K the two electrons tend to stay on the same side of the nucleus. In addition, the angular correlation quantum number K is related to the cosine of the interelectronic angle θ12 as K = −〈r cos θ12〉 where r denotes the radius of the inner electron. Physically, the larger the positive value of K, the value of −cosθ12 is closer to unity. These statements can be verified quantitatively in the framework of the SCUNC method by evaluating the radial expectation values \( \langle r^{−1} \rangle_n \) given by (in a.u) [6]

\[
\frac{1}{\langle r^{−1} \rangle_n} = \frac{Z^2}{2n^2} + \frac{Z^2}{2n^2} - E[\langle \theta, r \rangle_n^{3s+1l}] .
\] (7)

For the \( N = 3 \) threshold, we get

\[
\frac{1}{\langle r^{−1} \rangle_n} = \frac{Z^2}{18} + \frac{Z^2}{2n^2} - E[\langle \theta, r \rangle_n^{3s+1l}] .
\] (8)

Then

- The larger the positive value of K, the value of −cosθ12 is closer to unity and \( \theta_{12} \rightarrow \pi \). Subsequently, the interelectronic distance \( r_{12} \) increases and \( \langle r^{−1} \rangle_n \) decreases.

- For states with positive K, the two electrons tend to stay on the opposite sides of the nucleus, as a result the interelectronic distance \( r_{12} \) increases and \( \langle r^{−1} \rangle_n \) decreases.

- For states with negative K the two electrons tend to stay on the same side of the nucleus. The interelectronic distance \( r_{12} \) decreases while \( \langle r^{−1} \rangle_n \) increases.

So, quantitatively, \( \langle r^{−1} \rangle_n (K > 0) < \langle r^{−1} \rangle_n (K < 0) \).

Table 6 lists radial expectation values \( \langle r^{−1} \rangle_n \) for the \( 3\{0,2\}^3_3^31D°, 3\{2,0\}^1_3^11D^\ast, 3\{1,1\}^3_3^3\pi^\ast, 3\{2,0\}^3_3^31F^\ast, 3\{1,1\}^3_3^33P^e \) and \( 3\{−1,1\}^3_3^33P^e \) levels of some He-like ions (\( Z = 3-10 \)).

Comparison shows clearly that, for both \( 3\{0,2\}^3_3^31D°, 3\{2,0\}^1_3^11D^\ast \) (\( K = 0 \) and \( K = 2 \)), \( 3\{1,1\}^3_3^3\pi^\ast, 3\{2,0\}^3_3^31F^\ast \) (\( K = 1 \) and \( K = 2 \)), the radial expectation values \( \langle r^{−1} \rangle_n \) is lower for the greater value of K. As a result, \( r_{12} \) decreases and \( \theta_{12} \rightarrow \pi \) so −cosθ12 tends to unity. This confirms quantitatively that the larger the positive value of K, the value of −cosθ12 is closer to unity. Besides, for the \( 3\{1,1\}^3_3^33P^e \) and \( 3\{−1,1\}^3_3^33P^e \) levels where K takes the values 1 and −1.

Table 6. Present calculations of radial expectation values \( \langle r^{−1} \rangle_n \) (in a.u) for quantitative interpretation of the correlation quantum number K.
Table 6 shows clearly that, the radial expectation values \( \left\langle r_{12}^{-1} \right\rangle / 3 \) is lower for \( K = 1 \). This important result indicates again that \( \left\langle r_{12}^{-1} \right\rangle \) (\( K > 0 \)) < \( \left\langle r_{12}^{-1} \right\rangle \) (\( K < 0 \)) as demonstrated in the recent work of Sakho [6].

4. Conclusion

In this paper, accurate resonance energies of the \( \gamma(K, T, A)_{n}^{13}L^{\pi} \) Rydberg series of the helium-like ions (\( Z = 3-12 \)) are reported. Calculations are performing in the framework of the Screening constant by unit nuclear charge formalism. Good agreements are obtained with various literature data. In contrast with all the existing ab initio methods for which resonance energies cannot be calculated directed from analytical formula, it is demonstrated in this work the possibilities to report accurate resonance from a simple and single analytical formula. It should be underlined that, no resonance energies are listed in the NIST database for the \( N > 2 \) thresholds for many He-like systems. The present calculations may then be very useful for the NIST team as far as critical evaluation of atomic data relative to the doubly \( \gamma(K, T, A)_{n}^{13}L^{\pi} \) excited states in the Helium-like systems are concerned.

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