Variational Calculations for (ns²) ¹Sᵉ, (np²) ¹Dᵉ and (nd²) ¹Gᵉ Resonance States for He Isoelectronic Sequences below the n = 2, 3 and 4 Hydrogenic Thresholds

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Abstract

This work presents results of the different parameters which characterize the nonrelativistic Hamilton operator for the helium atoms allowing us to solve the Schrödinger equation. The total energy is decomposed into three terms allowing to separate the kinetic energy, the electrons-nucleus interaction energy and the electron-electron interaction energy of the ($2s^2$, $3s^2$ and $4s^2$) ¹Sᵉ, ($2p^2$, $3p^2$ and $4p^2$) ¹Dᵉ and ($3d^2$ and $4d^2$) ¹Gᵉ resonance singlet states of the helium isoelectronic sequences. The states have been defined by using special forms of the Hylleraas type wave functions. The calculations have been carried out in the framework of the variational method using configuration interaction basis states with a real Hamiltonian. The agreement of the energy value of other states between the present theoretical values available in the literature is excellent. But as for the comparison of the kinetic energies, the electrons-nucleus energies interaction and the electron-electron interaction energies, we note a slight difference with the theoretical values common in literature.

1. Introduction

Double photoionization occupies an important place because of the crucial role that electron-electron interaction plays in the ejection of two electrons by the photoabsorption of a single photon. Electron-electron correlation is also an essential feature in the process of simultaneous excitation and ionization when an

electron is ejected and the residual ion is in excited state. Many years ago, in helium atoms, all of the spectra transitions emitted by the atoms were visible and only one electron was in excited state. No spectra transition corresponding to the de-excitation of atoms with two electrons having been excited was observed. At the time, we did not have any light sources possessing photons with sufficient energies for double excitation of the atoms. It was in 1963, at the National Bureau of Standards (NBS) in Gaithersburg, that Madden and Codling [1] used the first light source with a continuous UV spectrum that was able to describe doubly excited helium atoms. The experimental observations of Madden and Codling allowing the identification of the painfully excited states of helium [1] [2] and the qualitative study of the correlation between two doubly excited electrons provided by the work of Cooper *et al.* [3] have been sources of deep inspiration for many researchers working in the study of doubly excited states (DES) of helium and helium-likes ions [4]-[9].

Over the years, several theoretical calculations have been developed for the descriptions of the doubly excited states, especially for the doubly excited states of helium and helium-like ions for which many experimental data have confirmed. A recent photoionization experiments have been performed by Morgan and Ederer [10] to observe resonance with excellent precision and Bizau *et al.* [11] have studied also the photoionization descriptions with excitation above the n = 2 threshold. On the theoretical part, different approaches have been used for that purpose by the theorists. Among these theoretical methods we can note: Berrington *et al.* [12] have used a six-state pseudostate close-coupling method, the photoionization process has been studied by a Feshbach projection method by Bhatia and Temkin [13], Salomonson *et al.* [14] have employed the many-body perturbation theory to study photoionization with excitation, Ojha [15] has applied multichannel quantum-defect theory to study these processes near the n=2 threshold, the variational method [16] [17], the screening constant by unit nuclear charge method [18] etc.

In general, combinations of functions are necessary in order to give a good description of doubly excited states. The wave functions are used in the incomplete hydrogenic product combined with the truncated diagonalization method, the Slater wave functions in the complex rotation method, the Hylleraas-type wave functions in the complex rotation method, the variational method and the diagonalization method. In the case of the complex rotation method, many authors use the Hylleraas-type wave functions for the intrashell doubly excited energies and width calculations. For the intershell doubly excited energies and width calculations of two electron systems, they use the Slater wave functions [5].

The present work is an extension of the earlier calculations of two-photon excitation and ionization energies of the Rydberg helium [7] [8]. Special forms of the Hylleraas-type wave functions constructed in the previous paper have been used for the intrashell doubly excited energies calculations of the helium-like ions. In this communication we reported, without the Slater wave functions, the total energy and the various parameters as the kinetic energy, the electrons-nucleus

interaction energy and the electron-electron interaction energy of the ($2s^2$, $3s^2$ and $4s^2$) $^1S^e$, ($2p^2$, $3p^2$ and $4p^2$) $^1D^e$ and ($3d^2$ and $4d^2$) $^1G^e$ resonance states of the helium isoelectronic sequences with Z = 2 - 10, by using the same special forms of Hylleraas type wave functions. The calculations have been carried out in the framework of the variational method using configuration interaction basis states with a real Hamiltonian. In the calculations we have neglected the Feshbach shifts. The aim of this work is to show the possibility of these special forms of Hylleraas-type wave functions to describe some intrashell singlet of doubly excited states of two electron atoms. This work allowed the use of small basis sets (13 terms) in the calculations.

The rest of this paper is arranged as follows: Section 2 presents the theoretical procedures used in this work. Section 3 is about the comparisons of our results with the other theoretical calculations data, through curves. Here also, we have no experimental data and there is not much theoretical data available, for comparisons. Finally, conclusion is drawn.

2. Method of Numerical Calculations

2.1. Hamiltonian and Wave Functions

The Schrödinger equation for the relative motion of the helium-like ion, which interacts with each other by a spherically symmetric potential, can be written as:

$$H\Phi(r_1, r_2) = E\Phi(r_1, r_2) \tag{1}$$

where H is the Hamilton operator for the helium atom we shall use the approximation is given by:

$$H = -\frac{\hbar}{2m}(\Delta_1 + \Delta_2) - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{|r_1 - r_2|}, \tag{2}$$

The vector r_1 and r_2 denote the positions of the two electrons, m the mass of an electron, e the elementary charge and Z the nuclear charge number, Δ_1 and Δ_2 the Laplace operator of the two electrons.

The Hamilton operator can be consists of three parts:

$$H = T + C + W, \tag{3}$$

where T, C and W are respectively the kinetic energy operator of the two electrons, the Coulomb interaction operator between the atomic nucleus and the two electrons and the Coulomb interaction operator between the two electrons:

$$T = -\frac{\hbar}{2m}(\Delta_1 + \Delta_2), \tag{4}$$

$$C = -\frac{Ze^2}{r_1} - \frac{Ze^2}{r_2}, \tag{5}$$

$$W = \frac{e^2}{|r_1 - r_2|}, \tag{6}$$

In this case of the Hamilton operator, all magnetic and relativistic effects together with the motion of the atomic nucleus are neglected.

In this article, $\Phi\left(\boldsymbol{r}_1,\boldsymbol{r}_2\right)$ are the trials non-orthogonal of two-electron wave functions that we have considered for the description of the intrashell singlet doubly excited states of the helium-like ions. There are special constructions of the incomplete hydrogenic wave functions and Hylleraas type wave functions as follows:

$$\Phi_{j,k,m}\left(\boldsymbol{r}_1,\boldsymbol{r}_2\right)=\chi_{j,k,m}\left(\boldsymbol{r}_1,\boldsymbol{r}_2\right)\varphi_{j,k,m}\left(\boldsymbol{r}_1,\boldsymbol{r}_2\right),\tag{7}$$

With

$$\varphi_{j,k,m}\left(\boldsymbol{r}_1,\boldsymbol{r}_2\right)=\left(r_1+r_2\right)^j\left(r_1-r_2\right)^k\left|\boldsymbol{r}_1-\boldsymbol{r}_2\right|^m\exp\left[-\lambda\left(r_1+r_2\right)\right],\tag{8}$$

which are Hylleraas ground state wave functions of the helium-like ions [19], including electron correlation effects; j, k, m are Hylleraas parameters with (j, k, $m \geq 0$), λ is a coefficient defined by

$$\lambda=\frac{Z}{\alpha n a_0},\tag{9}$$

where Z, α, a_0 and n are respectively the nucleus charge number, variational parameters, Bohr's radius and the principal quantum number.

These wave functions $\varphi_{j,k,m}\left(\boldsymbol{r}_1,\boldsymbol{r}_2\right)$ are not orthogonal.

The set of parameters (j, k, m) define the basis states (*i.e.* the configurations).

The even values of k define the symmetric wave functions describing the singlet states.

The wave functions $\Phi_{j,k,m}\left(\boldsymbol{r}_1,\boldsymbol{r}_2\right)$, are incomplete hydrogenic wave functions and can be expressed as follows:

$$\Phi_{n,l}\left(\boldsymbol{r}_1,\boldsymbol{r}_2\right)=\left(2r_12r_2\right)^l\left\{\sum_{\upsilon=0}^{\upsilon=n-l-1}\left[\left(n^2a_0^2\lambda^2\right)\left(2r_12r_2\right)\right]^\upsilon\right\}\left(r_1+r_2\right)^j\left(r_1-r_2\right)^k$$
$$\times\left|\boldsymbol{r}_1-\boldsymbol{r}_2\right|^m\exp\left[-\lambda\left(r_1+r_2\right)\right],\tag{10}$$

With

$n=\left(j,k,m\right)$: principal quantum number.

l: orbital angular moment.

The interesting feature in the wave functions $\Phi_{j,k,m}\left(\boldsymbol{r}_1,\boldsymbol{r}_2\right)$, is that they contain an electron correlation term: $\left|\boldsymbol{r}_1-\boldsymbol{r}_2\right|$, which represents the angular part of the wave functions instead of the spherical harmonic in the other Hylleraas type wave functions.

This electron correlation term plays an important role in our trial wave functions for the description of the intrashell singlet doubly excited states. The wave functions $\Phi_{j,k,m}\left(\boldsymbol{r}_1,\boldsymbol{r}_2\right)$ have also the advantage that, in the eigenvalue calculations E, the exhibition of a plateau and the convergence of the minima of the functions $\left(\mathrm{d}E/\mathrm{d}\alpha=0\right)$ arise quickly for small basis set (13 terms).

2.2. Calculation Procedures

The final form of the wave functions of the intrashell singlet doubly excited state including the correlation effects due to the mixing of configurations can be ex-

pressed as follows:

$$\psi_{n,l}\left(\boldsymbol{r}_1,\boldsymbol{r}_2\right)=\sum_n a_n \Phi_{n,l}, \tag{11}$$

where a_n are the eigenvectors which can be determined by solving the Schrödinger equation.

$$H\psi_{n,l}\left(\boldsymbol{r}_1,\boldsymbol{r}_2\right)=E\psi_{n,l}\left(\boldsymbol{r}_1,\boldsymbol{r}_2\right), \tag{12}$$

The representation of the Schrodinger equation on the non-orthogonal basis leads to the general eigenvalue equation:

$$\sum_{n'}\left(H_{n,n'}-EN_{n,n'}\right)a_{n'}=0, \tag{13}$$

with:

$$N_{n,n'}=N_{J,K,M}=\left\langle\psi_{n,l}\big|\psi_{n',l}\right\rangle, \tag{14}$$

$$H_{n,n'}=H_{J,K,M}=\left\langle\psi_{n,l}\big|H\big|\psi_{n',l}\right\rangle, \tag{15}$$

$$H_{n,n'}=H_{J,K,M}=\left\langle\psi_{n,l}\big|T+C+W\big|\psi_{n',l}\right\rangle, \tag{16}$$

$$H_{n,n'}=\left\langle\psi_{n,l}\big|T\big|\psi_{n',l}\right\rangle+\left\langle\psi_{n,l}\big|C\big|\psi_{n',l}\right\rangle+\left\langle\psi_{n,l}\big|W\big|\psi_{n',l}\right\rangle, \tag{17}$$

$$T_{n,n'}=T_{J,K,M}=\left\langle\psi_{n,l}\big|T\big|\psi_{n',l}\right\rangle=\left\langle T\right\rangle, \tag{18}$$

$$C_{n,n'}=C_{J,K,M}=\left\langle\psi_{n,l}\big|C\big|\psi_{n',l}\right\rangle=\left\langle C\right\rangle, \tag{19}$$

$$W_{n,n'}=W_{J,K,M}=\left\langle\psi_{n,l}\big|W\big|\psi_{n',l}\right\rangle=\left\langle W\right\rangle, \tag{20}$$

$$H_{J,K,M}=T_{J,K,M}+C_{J,K,M}+W_{J,K,M}=\left\langle E\right\rangle=\left\langle T\right\rangle+\left\langle C\right\rangle+\left\langle W\right\rangle, \tag{21}$$

Wherein $N_{J,K,M}$ are the matrix elements of normalisation factor, $H_{J,K,M}$ the matrix elements of Hamilton operator, $T_{J,K,M}$ the matrix elements of kinetic energy operator of the two electrons, $C_{J,K,M}$ the matrix elements of electrons-nucleus interaction energy operator and $W_{J,K,M}$ the matrix elements of electron-electron interaction energy operator.

For example, we present the result of the different parameters of $2s^2$ state:

- Matrix elements of normalisation factor:

$$\begin{aligned}
N_{J,K,M} =&\ \frac{2\pi^2}{M+2}\left(\frac{1}{K+1}-\frac{1}{K+3}-\frac{1}{K+M+3}+\frac{1}{K+M+5}\right)(J+K+M+5)!\left(\frac{1}{2\lambda}\right)^{J+K+M+6}\\
&+\frac{4\pi^2}{M+2}\left(na_0\lambda\right)^2\left(\frac{1}{K+1}-\frac{2}{K+3}+\frac{1}{K+5}-\frac{1}{K+M+3}+\frac{2}{K+M+5}\right.\\
&\left.-\frac{1}{K+M+7}\right)(J+K+M+7)!\left(\frac{1}{2\lambda}\right)^{J+K+M+8}\\
&+\frac{2\pi^2}{M+2}\left(na_0\lambda\right)^4\left(\frac{1}{K+1}-\frac{3}{K+3}+\frac{3}{K+5}-\frac{1}{K+7}-\frac{1}{K+M+3}+\frac{3}{K+M+5}\right.\\
&\left.-\frac{3}{K+M+7}+\frac{1}{K+M+9}\right)(J+K+M+9)!\left(\frac{1}{2\lambda}\right)^{J+K+M+10}\quad\text{for }K=0,2,4,6,\cdots\\
N_{J,K,M} =&\ 0\quad\text{for }K=1,3,5,7,\cdots
\end{aligned}$$

$$\tag{22}$$

- Matrix elements of electrons-nucleus interaction energy:

$$C_{J,K,M} = \frac{2\pi^2}{M+2}\left(\frac{1}{K+1} - \frac{1}{K+M+3}\right)(J+K+M+4)!\left(\frac{1}{2\lambda}\right)^{J+K+M+5}$$

$$+ \frac{16\pi^2}{M+2}(na_0\lambda)^2\left(\frac{1}{K+1} - \frac{1}{K+3} - \frac{1}{K+M+3} + \frac{1}{K+M+5}\right)(J+K+M+6)!\left(\frac{1}{2\lambda}\right)^{J+K+M+7}$$

$$+ \frac{8\pi^2}{M+2}(na_0\lambda)^4\left(\frac{1}{K+1} - \frac{2}{K+3} + \frac{1}{K+5} - \frac{1}{K+M+3} + \frac{2}{K+M+5}\right.$$

$$\left. - \frac{1}{K+M+7}\right)(J+K+M+8)!\left(\frac{1}{2\lambda}\right)^{J+K+M+9} \quad \text{for } K = 0,2,4,6,\cdots$$

$$C_{J,K,M} = 0 \quad \text{for } K = 1,3,5,7,\cdots$$

(23)

- Matrix elements of electron-electron interaction energy:

$$W_{J,K,M} = e^2 N_{J,K,M-1} \tag{24}$$

- Matrix elements of kinetic energy:

$$T_{J,K,M} = 2\left(\lambda^2 N_{J,K,M} - J\lambda N_{J-1,K,M} + jj'N_{J-2,K,M} + kk'N_{J,K-2,M} + mm'N_{J,K,M-2}\right)$$

$$+ \frac{1}{2}\left[-M\lambda\left(C_{J,K,M} - C_{J,K+2,M-2}\right) + (mj' + jm')\left(C_{J-1,K,M} - C_{J-1,K+2,M-2}\right)\right.$$

$$\left. + (mk' + km')\left(C_{J+1,K,M-2} - C_{J-1,K,M}\right)\right]$$

(25)

All the other states are calculated with this same way.

The intrashell singlet doubly excited wave functions were found in the basis containing the configurations with the following condition for the Hylleraas parameters $j + k + m \leq 3$, corresponding to the basis dimension $D = 13$.

In order to obtain the minimum eigenvalue in which we are interested in the calculations are carried out for various values of the parameter α.

The eigenvalues E obtained in the present calculations follow the Hylleraas-Undheim theorem [20] and do not include the Feshbach shifts because of the use of the incomplete basis sets of the wave functions.

According to the Hylleraas-Undheim theorem [20], a good approximation for the eigenvalues is obtained when the minima of the functions $(dE/d\alpha = 0)$ converge with increasing values of the dimension D and when the functions exhibit a plateau.

3. Results and Discussions

In Figures 1-8, we show the variation, of the kinetic energies $\langle T \rangle$, the electrons-nucleus interaction energies $\langle C \rangle$, the electron-electron interaction energies $\langle W \rangle$ and the total energies $\langle E \rangle$ of the present work for $(2s^2)$ $^1S^e$, $(3s^2)$ $^1S^e$, $(4s^2)$ $^1S^e$, $(2p^2)$ $^1D^e$, $(3p^2)$ $^1D^e$, $(4p^2)$ $^1D^e$, $(3d^2)$ $^1G^e$ and $(4d^2)$ $^1G^e$ states of helium-like ions with Z = 2 - 10.

We compare in the Figure 9 and Figure 10, our results of the kinetic energies $\langle T \rangle$ for $(2s^2)$ $^1S^e$ and $(3s^2)$ $^1S^e$ states of helium-like ions (Z = 2 - 10) with the
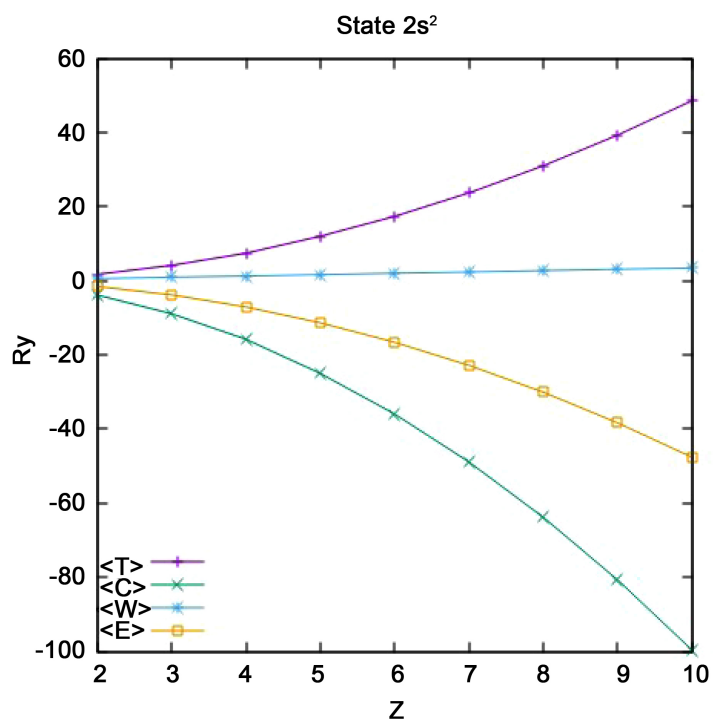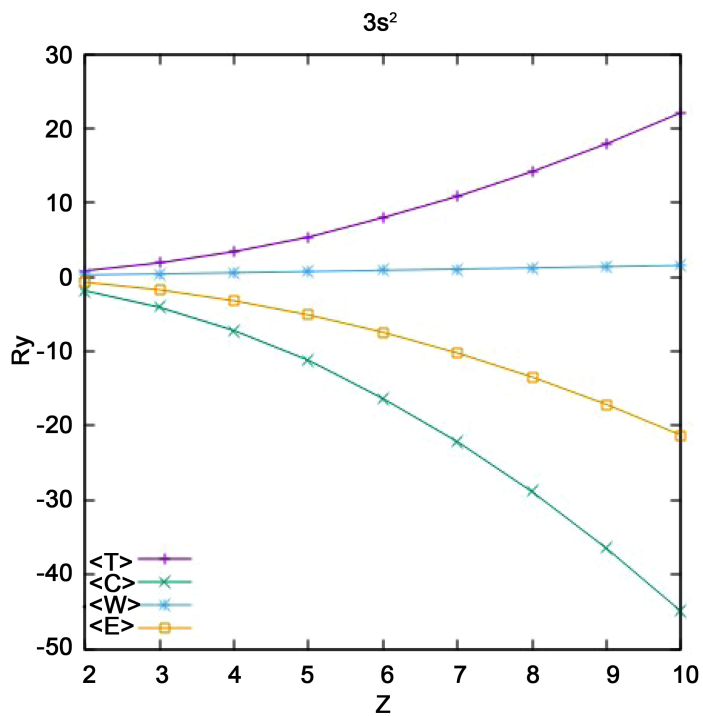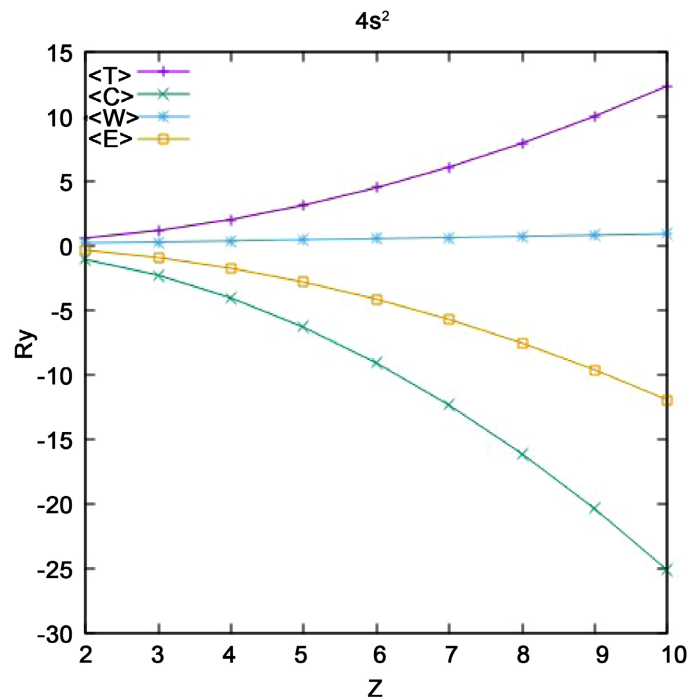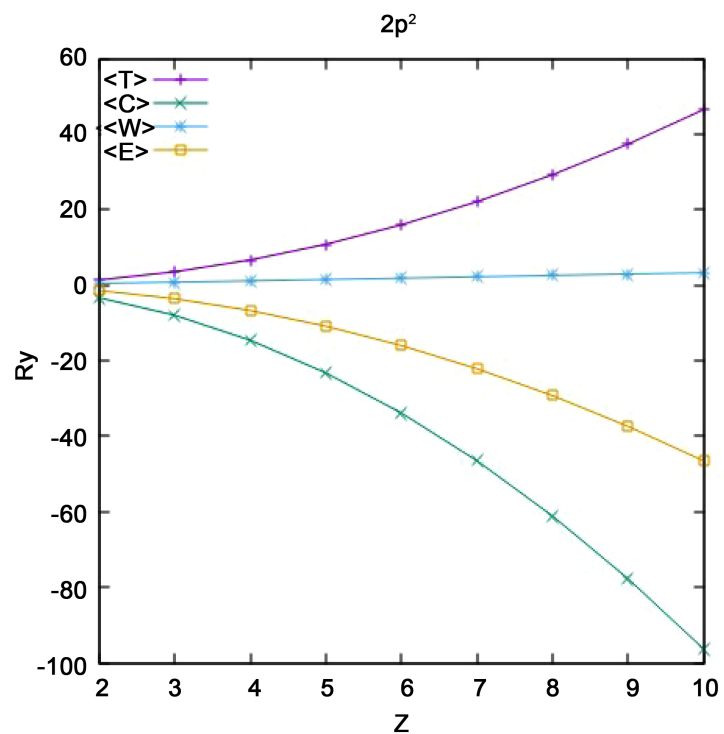
State 2s²

Figure 1. Variation of the kinetic energies $\langle T \rangle$, the electron-nucleus energies $\langle C \rangle$, the electron-electron energies $\langle W \rangle$ and the total energies $\langle E \rangle$ of the present work for (2s²) ¹Sᵉ state of helium-like ions (Z = 2 - 10).
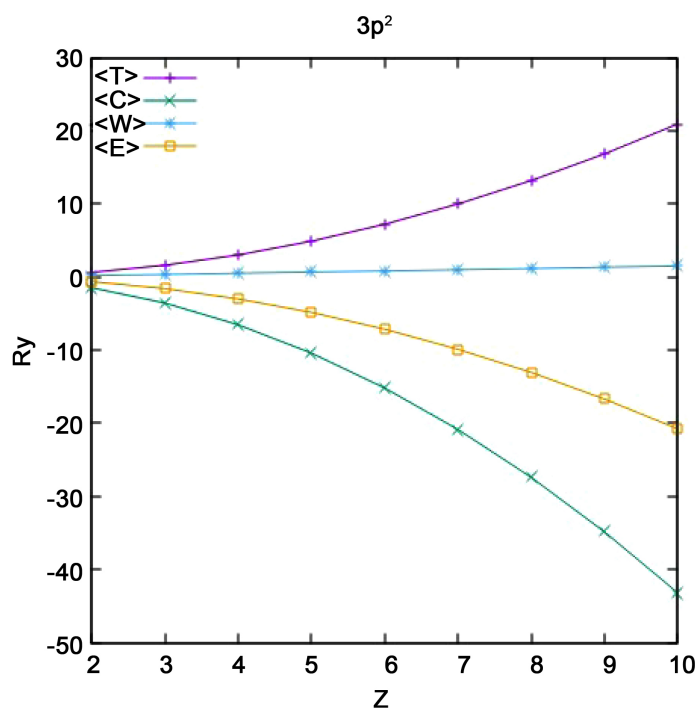
3s²

Figure 2. Variation of the kinetic energies $\langle T \rangle$, the electron-nucleus energies $\langle C \rangle$, the electron-electron energies $\langle W \rangle$ and the total energies $\langle E \rangle$ of the present work for (3s²) ¹Sᵉ state of helium-like ions (Z = 2 - 10).
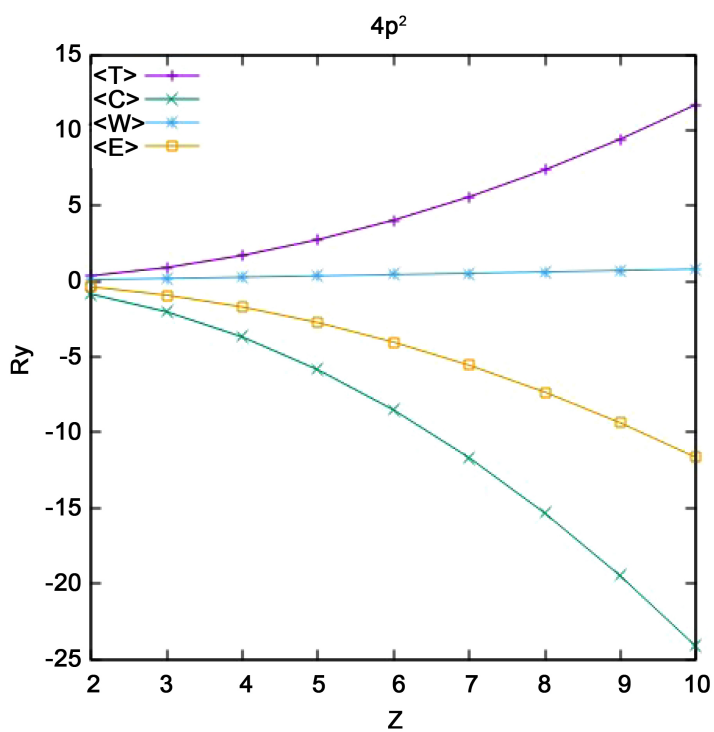
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4s²

Figure 3. Variation of the kinetic energies $\langle T \rangle$, the electron-nucleus energies $\langle C \rangle$, the electron-electron energies $\langle W \rangle$ and the total energies $\langle E \rangle$ of the present work for (4s²) ¹Sᵉ state of helium-like ions (Z = 2 - 10).

2p²

Figure 4. Variation of the kinetic energies $\langle T \rangle$, the electron-nucleus energies $\langle C \rangle$, the electron-electron energies $\langle W \rangle$ and the total energies $\langle E \rangle$ of the present work for (2p²) ¹Dᵉ state of helium-like ions (Z = 2 - 10).
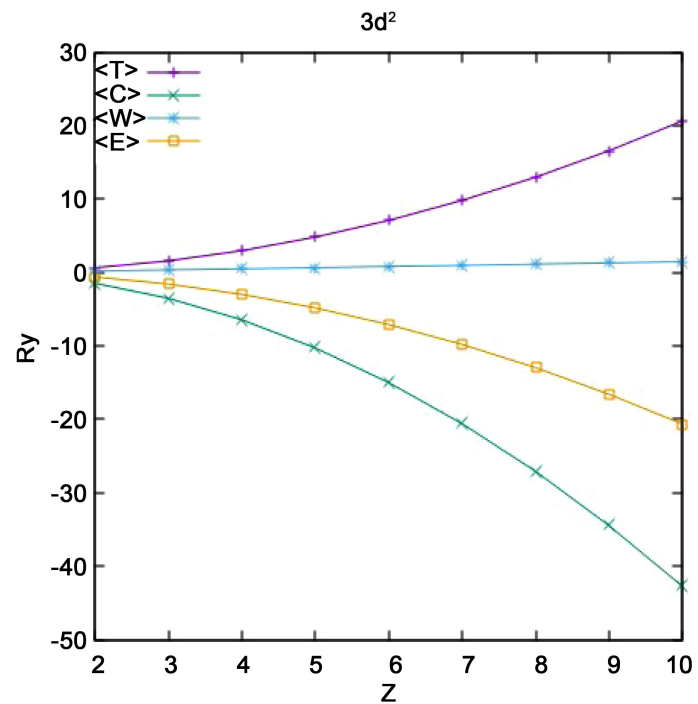
Figure 5. Variation of the kinetic energies $\langle T \rangle$, the electron-nucleus energies $\langle C \rangle$, the electron-electron energies $\langle W \rangle$ and the total energies $\langle E \rangle$ of the present work for $(3p^2)$ $^1D^e$ state of helium-like ions (Z = 2 - 10).
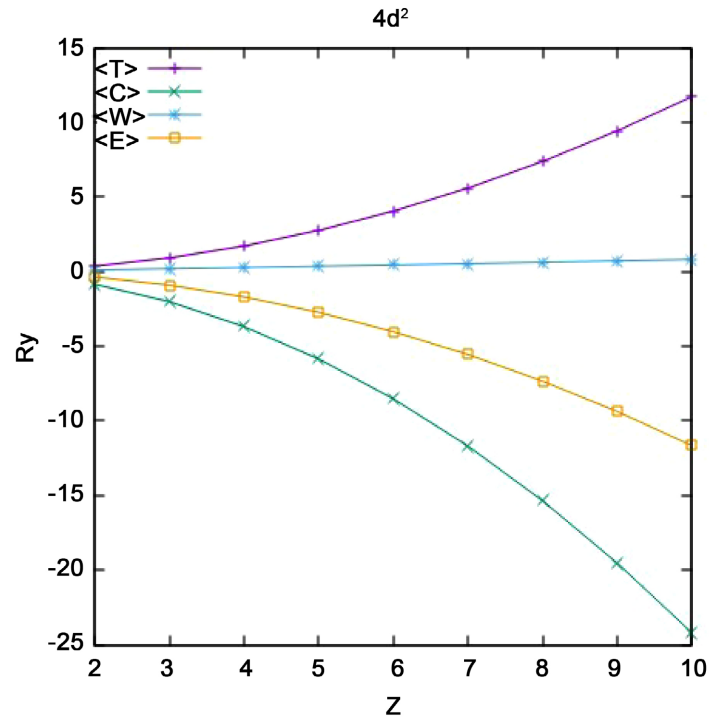

Figure 6. Variation of the kinetic energies $\langle T \rangle$, the electron-nucleus energies $\langle C \rangle$, the electron-electron energies $\langle W \rangle$ and the total energies $\langle E \rangle$ of the present work for $(4p^2)$ $^1D^e$ state of helium-like ions (Z = 2 - 10).

Figure 7. Variation of the kinetic energies $\langle T \rangle$, the electron-nucleus energies $\langle C \rangle$, the electron-electron energies $\langle W \rangle$ and the total energies $\langle E \rangle$ of the present work for $(3d^2)$ $^1G^e$ state of helium-like ions (Z = 2 - 10).

Figure 8. Variation of the kinetic energies $\langle T \rangle$, the electron-nucleus energies $\langle C \rangle$, the electron-electron energies $\langle W \rangle$ and the total energies $\langle E \rangle$ of the present work for $(4d^2)$ $^1G^e$ state of helium-like ions (Z = 2 - 10).
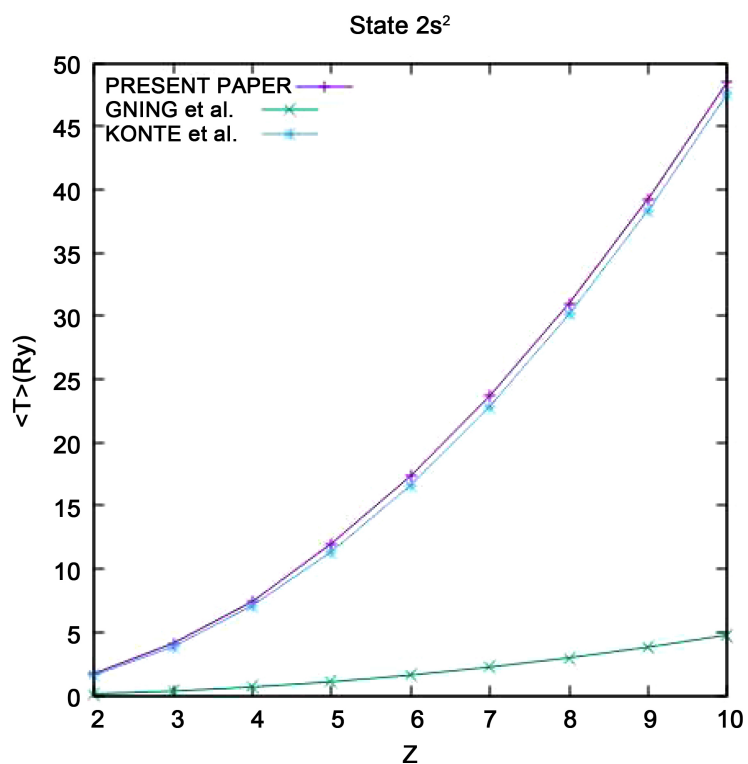
Figure 9. Comparison of the kinetic energies $\langle T \rangle$ of the present work with other results for $(2s^2)$ $^1S^e$ state of helium-like ions (Z = 2 - 10).
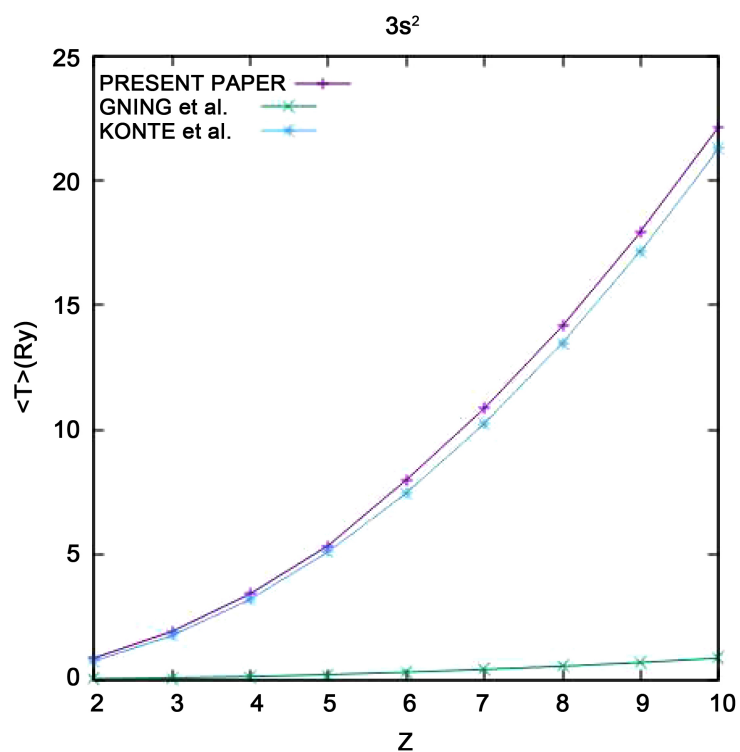

Figure 10. Comparison of the kinetic energies $\langle T \rangle$ of the present work with other results for $(3s^2)$ $^1S^e$ state of helium-like ions (Z = 2 - 10).

theoretical values of Gning *et al.* [21], Konté *et al.* [22] which have use respectively the complex rotation method implemented in Scilab and the method of stabilization using correlated Hylleraas-type wave functions. We note that the kinetic energy increases when Z is large and it varies like a parabolic function. We note also a little disagreement between our results and the other theoretical calculations of Konté *et al.* [22] when Z increases and a big difference with the results of Gning *et al.* [21]. The increase of the nucleus charge number Z leads more kinetic energy.

Figure 11 and **Figure 12** compare our results of the electrons-nucleus energies $\langle C \rangle$ for (2s²) ¹Sᵉ and (3s²) ¹Sᵉ states of helium-like ions (Z = 2 - 10) with the theoretical values of Gning *et al.* [21]. and Konté *et al.* [22]. We find that the variational of $\langle C \rangle$ looks like a hyperbolic function and it is substantially opposite to twice $\langle T \rangle$. It is seen that; a little discrepancy appears when the charge number increases between our results and the theoretical calculations of Konté *et al.* [22] and a big gap with Gning *et al.* [21] results. The absolute value of electron-nucleus interaction energy increase as the nucleus charge number Z.

Figure 13 and **Figure 14** contain comparison electron-electron interaction energies $\langle W \rangle$ of the present work with results of Gning *et al.* [21] and Konté *et al.* [22] for (2s²) ¹Sᵉ and (3s²) ¹Sᵉ states of helium-like ions (Z = 2 - 10). We see $\langle W \rangle$ is linear function of Z. Comparison done with results of Gning *et al.* [21] and Konté *et al.* [22] shows a discrepancy when Z increases. This is the only
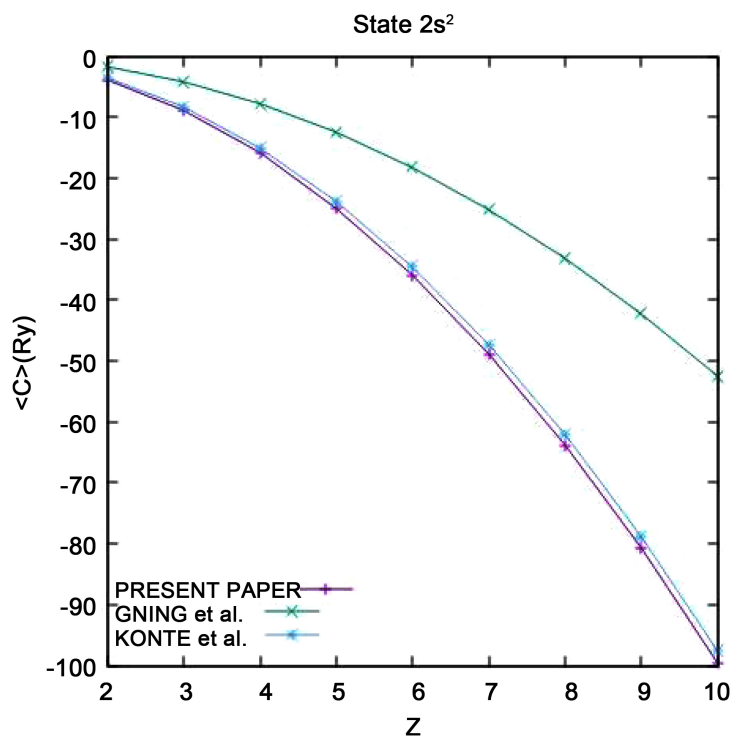

Figure 11. Comparison of the electron-nucleus energies $\langle C \rangle$ of the present work with other results for (2s²) ¹Sᵉ state of helium-like ions (Z = 2 - 10).
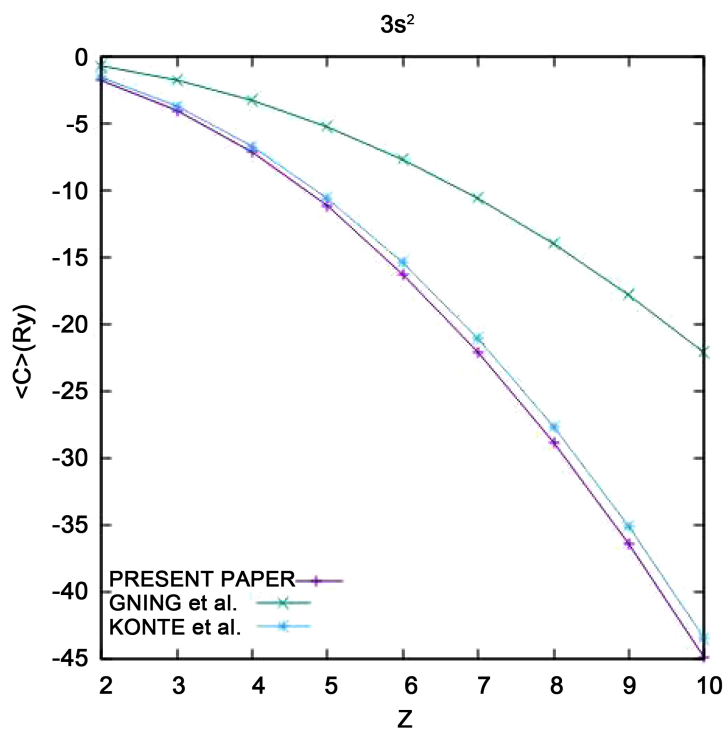
Figure 12. Comparison of the electron-nucleus energies $\langle C \rangle$ of the present work with other results for $(3s^2)$ $^1S^e$ state of helium-like ions (Z = 2 - 10).
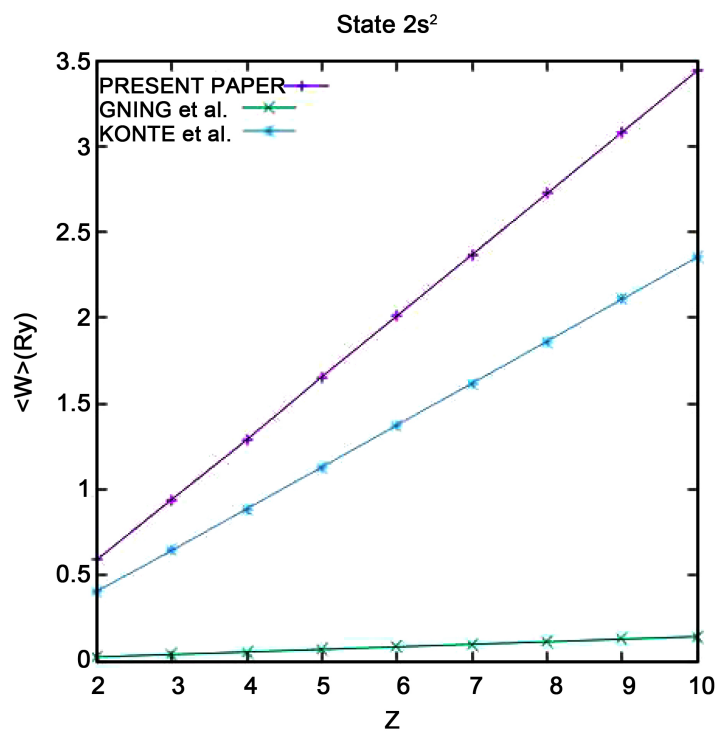

Figure 13. Comparison of the electron-electron energies $\langle W \rangle$ of the present work with other results for $(2s^2)$ $^1S^e$ state of helium-like ions (Z = 2 - 10).
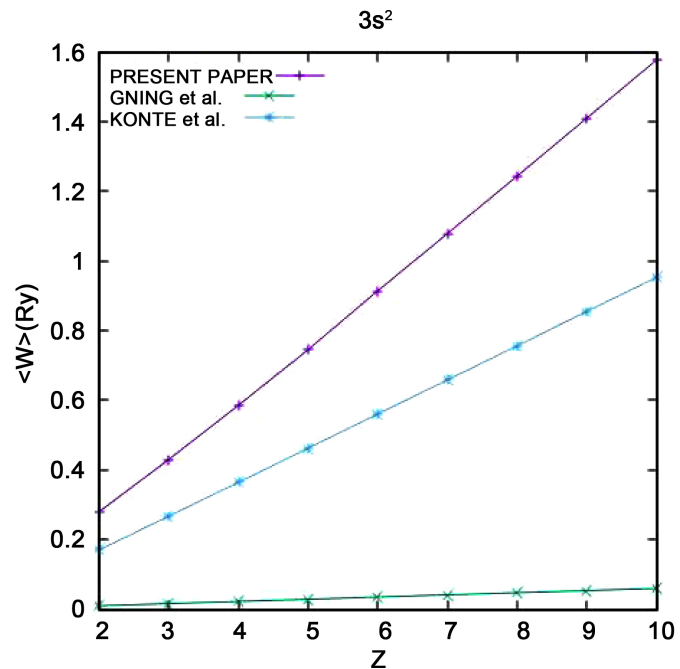
Figure 14. Comparison of the electron-electron energies $\langle W \rangle$ of the present work with other results for $(3s^2)$ $^1S^e$ state of helium-like ions (Z = 2 - 10).
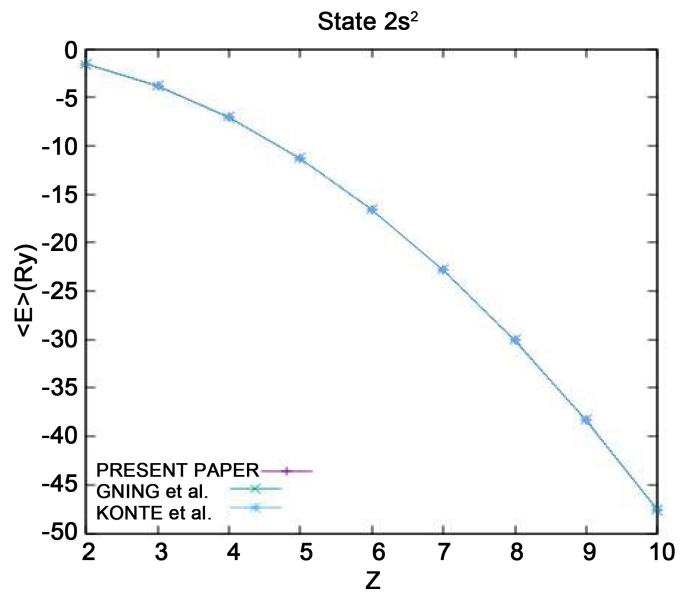

Figure 15. Comparison of the total energies $\langle E \rangle$ of the present work with other results for $(2s^2)$ $^1S^e$ state of helium-like ions (Z = 2 - 10).

comparison where we have a gread disagreement with the results of Konté *et al.* [22]. Electron-electron correlation is essential for the process of excitation and ionization and is gread when the nucleus charge number Z increase.

A comparison is made in **Figure 15** and **Figure 16** with the total energies of
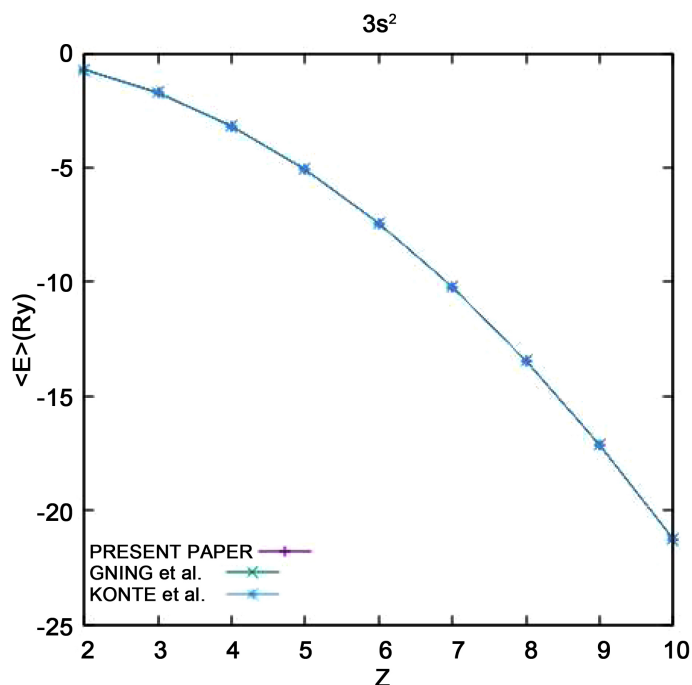
Figure 16. Comparison of the total energies $\langle E \rangle$ of the present work with other results for $(3s^2)$ $^1S^e$ state of helium-like ions (Z = 2 - 10).

Gning *et al.* [21] and Konté *et al.* [22] for $(2s^2)$ $^1S^e$ and $(3s^2)$ $^1S^e$ states of helium-like ions up to Z = 10. We note generally a good agreement between our results with those of Gning *et al.* [21] and Konté *et al.* [22].

4. Conclusion

We have estimated separately, using special forms of Hylleraas-type wave functions, the kinetic energies, the electrons-nucleus interaction energies, the electron-electron interaction energies and the total energies for (ns^2) $^1S^e$, (np^2) $^1D^e$ and (nd^2) $^1G^e$ resonance states for He isoelectronic sequences below the n = 2, 3 and 4 hydrogenic thresholds up to Z = 10. The calculations have been done in the framework of the variation method using configuration interaction basis states with a real Hamiltonian. Ours results for total energies are in good agreement with cited theoretical literatures values with other methods. For the kinetic energies and the electrons-nucleus interaction energies, we note a slight disagreement between our results and those of the other calculations. For the electron-electron interaction energies, this is the only comparison where we have a great disagreement with the other results. In a general way, we have presented in this paper satisfactory results which will be beneficial for theoretical and experimental research. Examples for other states as $nlnl'$ ($l \neq l'$) will be considered in the future.

Data Availability Statement

This manuscript has no associated data or the data will not be deposited. [Authors' comment: Data are available upon request.]

Conflicts of Interest

The author declares no conflicts of interest regarding the publication of this paper.

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