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Energies and electron correlation effects in two-electron doubly excited (nl)^2 states

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Abstract. Energies of singlet doubly excited states $2p^2\ ^1$D, $3d^2\ ^1$G, $4f^2\ ^1$I of He isoelectronic series are calculated in the framework of the variational method by using Hylleraas-type wave functions and a real Hamiltonian. The results obtained show quantitatively the importance of electron correlation effects in the doubly excited states and they are in good agreement with some experimental data and other theoretical results.

PACS. 31.25.Jf Electron-correlation calculations for atoms and ions: excited states

1 Introduction

Theoretical investigations in two-electron doubly excited states (DES) are of great interest in connection with the understanding of collisional and radiational processes which take place in hot astrophysical and laboratory plasma [1–3].

The main problem in the theoretical study of DES is connected with the correlated motion of highly-excited electrons in the field of a nucleus of charge Z [4–9]. Greatest interest have been concentrated on studying symmetric DES $(nl)^2$ with both excited electrons having equal values of principal quantum number n. It has been shown that in the description of such states, electron correlation plays a dominant role [10–16]. In addition it has been demonstrated that one of the manifestations of the electron correlation in the $(nl)^2$ doubly excited states is the existence of quasi-molecular rotational structure in the spectra of He isoelectronic series [14–16]. Theoretical investigations of $(nl)^2$ doubly excited states are performed by using various methods. The projection operator method [11,12] and group theoretical methods [14–16] have been used for the calculations of the energies of the $2s^2$, $2p^2$ states in helium atom. Time independent variational perturbation theory was applied for the calculations of the total energies of the $2s^2$, $2p^2$ and $3d^2$ states in He, Li$^+$, Be^{2+} and B^{3+} [17]. The correlation part of the energies for the $2s^2$, $2p^2$, $3s^2$, $3p^2$, $3d^2$ states in He isoelectronic series have been investigated by using perturbation theory [18]. The two-electron dipole approximation [19,20] was performed for the study of the characteristics of $(ns)^2$ states with $n \leq 5$. In most of these works, only the total energies have been calculated and the results have been reported for a limited number of He isoelectronic series and for low values of the principal quantum number n.

In this paper, following the work of Schmid *et al.* [21] for helium ground state, we have calculated the total energies of the singlet doubly excited $2p^2\ ^1$D, $3d^2\ ^1$G and $4f^2\ ^1$I states of He isoelectronic series with $Z \leq 12$. In addition, for the first time in our knowledge, we have made a quantitative evaluation of the magnitude of electron correlation in such states by calculating it together with the kinetic energies of the two electrons, the Coulomb electron-nucleus interaction energies and the Coulomb electron-electron interaction energies. Our calculations are made in the framework of the variational method with configuration interaction basis wave functions of Hylleraas-type in the field of real Hamiltonian.

In Section 2 we present the theoretical procedure applied in this work.

In Section 3 the presentation and the discussion of our results are made. A comparison of our calculations with available experimental data and other theoretical calculations is also made.

2 Theory

We have constructed the basis wave functions for each singlet $2p^2$, $3d^2$, and $4f^2$ states as follows:

$$\Phi_{jkmn}(\mathbf{r}_1,\mathbf{r}_2) = (2r_1 2r_2)^{n-1}(r_1+r_2)^j(r_1-r_2)^k \times |\mathbf{r}_1-\mathbf{r}_2|^m \exp[-\lambda(r_1+r_2)] \quad (1)$$

where the vectors $\mathbf{r}_1$ and $\mathbf{r}_2$ denote the positions of the two electrons; the abbreviations r_1 and r_2 are used for $|\mathbf{r}_1|$ and $|\mathbf{r}_2|$; j, k, m are Hylleraas parameters with (j, k, $m \geq 0$), n is the principal quantum number and λ is a coefficient

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defined by: $\lambda = Z/\alpha n r_0$ where Z, α, r_0 are respectively the nucleus charge number, variation parameter and Bohr's radius. The set of parameters $(j,\, k,\, m)$ define the basis states (*i.e.* the configurations).

The final form of the wave function of the singlet doubly excited state including the correlation effects due to the mixing of configurations can be expressed as follows:

$$\Psi_n(\mathbf{r}_1,\, \mathbf{r}_2) = \sum_{jkm} a_{jkm}\, \Phi_{jkmn}\, (\mathbf{r}_1,\, \mathbf{r}_2), \tag{2}$$

where the coefficients a_{jkm} are determined by solving the Schrödinger equation:

$$H\,\Psi_n(\mathbf{r}_1,\, \mathbf{r}_2) = E\,\Psi_n(\mathbf{r}_1,\, \mathbf{r}_2), \tag{3}$$

where the Hamilton operator H has the form:

$$H = T + C + W, \qquad \text{with} \tag{4}$$

$$T = \frac{-\hbar^2}{2m}\,(\Delta_1 + \Delta_2);\ C = -\left(\frac{Ze^2}{r_1} + \frac{Ze^2}{r_2}\right);$$

$$W = \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|}, \tag{5}$$

where T is the kinetic energy, C is the Coulomb potential between the atomic nucleus and the two electrons, W is the Coulomb interaction between electrons. In the Hamilton operator we have neglected all magnetic and relativistic effects together with the motion of the atomic nucleus. In what follows for the sake of brevity we shall denote the triad of Hylleraas parameters $(j,\, k,\, m)$ by q.

The representation of the Schrödinger equation on the non-orthogonal basis leads to the general eigenvalue equation [21,22]:

$$\sum_{q'} \left(H_{nqq'} - EN_{nqq'}\right) a_{q'} = 0, \tag{6}$$

$$\text{with} \qquad N_{nqq'} = \langle \Phi_{nq} | \Phi_{nq'} \rangle, \tag{7}$$

$$H_{nqq'} = \langle \Phi_{nq} | H | \Phi_{nq'} \rangle, \tag{8}$$

where $N_{nqq'}$ is the normalisation factor and $H_{nqq'}$ the matrix elements of Hamilton operator.

3 Results and discussion

We have performed our calculations as follows. The singlet doubly excited wave function was carried out in the basis containing the configurations with the following conditions for the Hylleraas parameters: $(j,\, k,\, m \geq 0)$ and $j+k+m \leq 3$. Due to the symmetry of the wave functions only even values are allowed for k.

Our calculations are carried out in 3×3, 6×6, 10×10 and 13×13 bases with the following values of the parameters (j,k,m):

$$(0,2,0),(1,2,0),(0,2,1) \quad \text{for the dimension} \quad D = 3;$$

$$(0,2,0),(0,0,2),(2,0,1),(1,2,0),(0,2,1),(0,0,3) \quad \text{for the dimension } D = 6;$$

$$(1,0,1),(0,2,0),(2,0,0),(0,0,2),(1,0,2),(2,0,1),(1,2,0),(0,2,1),(3,0,0),(0,0,3) \quad \text{for the dimension } D = 10;$$

$$(0,0,0),(0,0,1),(1,0,0),(1,0,1),(0,2,0),(2,0,0),(0,0,2),(1,0,2),(2,0,1),(1,2,0),(0,2,1),(3,0,0),(0,0,3) \quad \text{for the dimension } D = 13.$$

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

Figures 1–3 show the plots of the energy $E = f\,(\alpha,\, D)$ as a function of the parameter α and the dimension D. These plots concern the helium atom and are performed for the $2p^2\ {}^1$D, $3d^2\ {}^1$G, and $4f^2\ {}^1$I states. According to Hylleraas and Undheim theorem [21,22], a good approximation for the eigenvalues is obtained when the minima of the functions ($\mathrm{d}E/\mathrm{d}\alpha = 0$) converge with increasing values of D and when the functions exhibit a plateau. As long as the functions exhibit no plateau and as long as the minima of the functions do not converge with increasing values of D, one has not yet found a good approximation. In our calculations the exhibition of a plateau and the convergence of the minima arise when $D \geq 10$. This could be seen from the figures where there is a close similarity of the plots for $D = 10$ and $D = 13$. This similarity could be explained by the relatively weak contribution of the configurations (0, 0, 0); (0, 0, 1); (1, 0, 0) to the calculations of the eigenvalues. It is important to notice that we have obtained a good approximation for the eigenvalues with a relatively small dimension of the basis ($D = 13$) in comparison for example to the complex rotation method in which the dimension of the basis is often more than 100 [24].

In Table 1, we present the results of our calculations for the singlet doubly excited $2p^2\ {}^1$D, $3d^2\ {}^1$G, and $4f^2\ {}^1$I states. From these results, one can see that the virial theorem is satisfied: $-2\,T = C + W$. This shows the relatively good accuracy obtained for the values of the energies of atomic systems studied in this work. We can notice that the kinetic energy T and the correlation energy between the two electrons W increase with the nuclear charge number Z, and decrease when the principal quantum number n increases. These results point out that the electron correlation effects in the doubly excited states induce the decrease of the probability of electrons to be near the nucleus, as mentioned by Arias de Saavedra *et al.* [23]. On the other hand, for low values of Z ($Z \leq 3$) and with increasing principal quantum number n, the ratio W/C is quite important. That means that each electron is less and less attracted by the nucleus with increasing electron-electron interaction. Therefore, the two electrons tend to go far from each other so that they could be located on opposite sides of the nucleus forming a kind of linear symmetric molecular structure. This result is in good agreement

Table 1. Kinetic energies $\langle T \rangle$, Coulomb binding energies $\langle C \rangle$, Coulomb interaction energies between the two electrons $\langle W \rangle$, and total energies E for doubly excited states $2p^2\ ^1$D, $3d^2\ ^1$G and $4f^2\ ^1$I ($Z \leq 12$). The values are reported in eV.

States			Z										
			2	3	4	5	6	7	8	9	10	11	12
$2p^2\ ^1$D	Present work	$\langle T \rangle$	19.1857	48.3952	91.1523	147.4867	217.4159	300.9364	398.0581	508.7855	633.1135	771.0457	922.5827
		$\langle C \rangle$	–44.9144	–107.9254	–198.1718	–315.6455	–460.3457	–632.2593	–831.3910	–1057.7419	–1311.3052	–1592.083	–1900.0747
		$\langle W \rangle$	6.5426	11.1346	15.8672	20.6713	25.5163	30.3863	35.2730	40.1713	45.0779	49.9908	54.9083
		E	–19.1859	–48.3954	–91.1522	–147.4873	–217.4134	–300.9365	–398.0597	–508.7851	–633.1138	–771.0465	–922.5837
	Others works	E^a	–18.6781	–46.1327	–88.5697	–144.5834							
		E^b	–19.1135										
		E^c	–19.1026										
$3d^2\ ^1$G	Present work	$\langle T \rangle$	8.5825	21.5402	40.4984	65.4575	96.4386	133.4553	176.5076	225.5998	280.7332	341.9087	409.1301
		$\langle C \rangle$	–19.9774	–47.8417	–87.8028	–139.8477	–203.9885	–280.2318	–368.5726	–469.0116	–581.5475	–706.1796	–842.9100
		$\langle W \rangle$	2.8107	4.7518	6.8061	8.9328	11.1091	13.3203	15.5566	17.8115	20.0805	22.3606	24.6493
		E	–8.5841	–21.5496	–40.4983	–65.4573	–96.4406	–133.4561	–176.5083	–225.6002	–280.7337	–341.9102	–409.1305
	Others works	E^a	–8.4798	–19.8669	–38.6692	–63.4976							
		E^d	–8.3546										
$4f^2\ ^1$I	Present work	$\langle T \rangle$	4.8867	12.2182	22.8897	36.9541	54.3769	75.1957	99.3951	126.9939	157.9827	192.3679	230.1507
		$\langle C \rangle$	–11.3218	–27.0098	–49.4498	–78.7011	–114.7259	–157.5622	–207.1921	–263.6331	–326.8741	–396.9203	–473.7716
		$\langle W \rangle$	1.5484	2.5755	3.6617	4.7972	5.9693	7.1721	8.3988	9.6452	10.9075	12.1828	13.4691
		E	–4.8866	–12.2160	–22.8983	–36.9497	–54.3796	–75.1943	–99.3981	–126.9939	–157.9838	–192.3694	–230.1518

[a]: D. Ray [17]; [b]: Hicks *et al.* [13]; [c]: Bhatia *et al.* [12]; [d]: Herrick *et al.* [14].

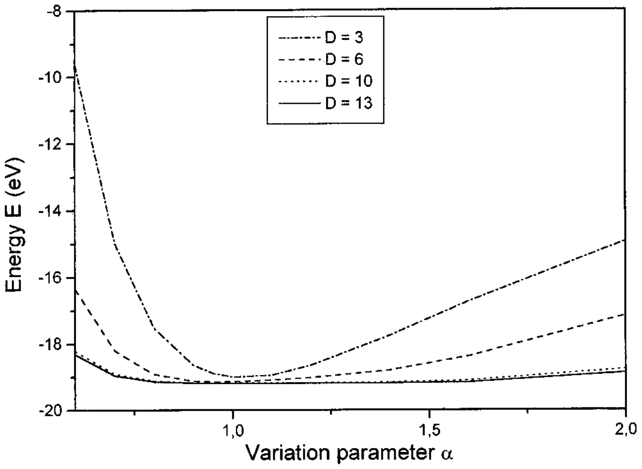

Fig. 1. Plots $E = f(\alpha)$ of the energy E in terms of the variation parameter α for the dimensions 3, 6, 10, 13 of the helium $2p^2\ {}^1\mathrm{D}$ state. The close similarity of the plots for $D = 10$ and $D = 13$ shows the convergence of the minima when $D \geq 10$.

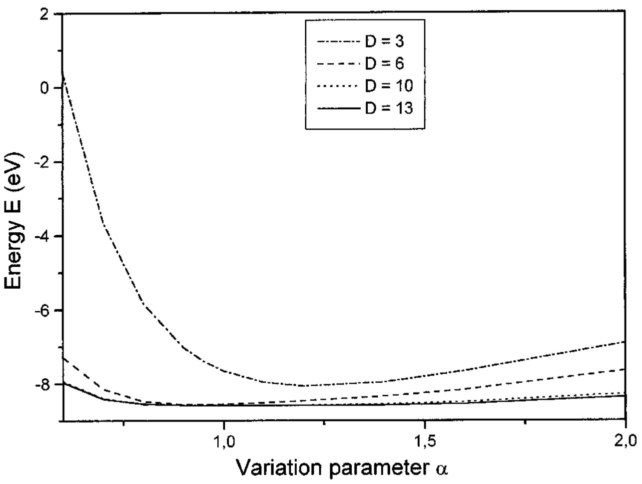

Fig. 2. Plots $E = f(\alpha)$ of the energy E in terms of the variation parameter α for the dimensions 3, 6, 10, 13 of the helium $3d^2\ {}^1\mathrm{G}$ state. The close similarity of the plots for $D = 10$ and $D = 13$ shows the convergence of the minima when $D \geq 10$.

with one aspect of electron correlation pointed out by Kellman and Herrick [16]: the resemblance of the atomic levels to the rotational spectrum of the linear triatomic XYX molecule, with X as an electron and Y as the nucleus. This resemblance becomes progressively worse and disappears when Z increases and when n decreases.

Concerning the total energies of the $2p^2\ {}^1\mathrm{D}$ and $3d^2\ {}^1\mathrm{G}$ states of He, the present calculations are in good agreement with experimental data of Hicks [13], and theoretical results obtained by Bhatia [12] and Herrick *et al.* [14].

For the Li^{+}, Be^{2+}, and B^{3+} ions there is some difference between our results and those obtained by Ray and Mukherjee [17]. This difference could be explained by the choice of the angular part of the wave functions introduced by these authors in their calculations.

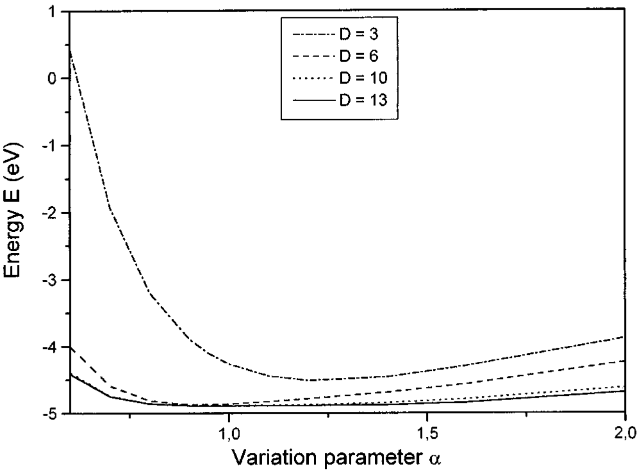

Fig. 3. Plots $E = f(\alpha)$ of the energy E in terms of the variation parameter α for the dimensions 3, 6, 10, 13 of the helium $4f^2\ {}^1\mathrm{I}$ state. The close similarity of the plots for $D = 10$ and $D = 13$ shows the convergence of the minima when $D \geq 10$.

For the other atomic systems with the nuclear charge $Z > 5$ and for the doubly excited $4f^2\ {}^1\mathrm{I}$ states, there are no experimental and theoretical data in our knowledge in the literature.

4 Conclusion

With a relatively small dimension of the basis functions and using Hylleraas-type wave functions, we have obtained a quantitative and qualitative estimation of electron correlation effects in singlet doubly excited states in helium atom and some helium-like ions. Our calculations for the total energies of the $2p^2\ {}^1\mathrm{D}$, $3d^2\ {}^1\mathrm{G}$ doubly excited singlet states of He are in good agreement with existing experimental data and other theoretical results. Relatively good, accurate values for the energies were obtained also for the $2p^2\ {}^1\mathrm{D}$, $3d^2\ {}^1\mathrm{G}$ doubly excited singlet states of helium-like ions with $Z \leq 12$. The results that we have obtained confirm that a relatively simple theoretical procedure could be used for adequate calculations and understanding of electron correlation effects in doubly excited two-electron states.

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