Precise Variational Calculation For The Doubly Excited State \((2p^2)^3P^e\) of Helium.

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Abstract

Highly precise variational calculations of non-relativistic energies of the \((2p^2)^3P^e\) state of Helium atom are presented. We get an upper bound energy \(E = -0.71050015565678\) a.u., the lowest yet obtained.

1 Introduction

Multiply excited energy states in atoms have been the subject of many experimental and theoretical investigations. Specially doubly excited states (DES) for neutral helium is particularly important as the DES provide a fundamental testing ground of the accuracy of the theoretical treatment. The review article of Holøien and Fano gives a detailed list of references.

A large number of DES of neutral helium can auto-ionize to the continuum above the \(1s(2S)\) ground state of \(He^+\). Besides, there are also non-auto-ionizing doubly excited states in helium. These exactly quantized DES states decay to the lower excited states through electric dipole interaction giving rise to sharp spectral line. It is worthwhile to mention that relativistically these states may auto-ionize, but the auto-ionization life times are still appreciably longer than the mean radiative life times of the allowed electric dipole transition.

Compton and Boyce, Kruger, Whiddington and Priestley are the pioneers to observe such exactly quantized DES of helium. Among such non-auto-ionizing doubly excited levels in helium, the \((2p^2)^3P^e\) state is the lowest lying P-state of even parity. The interpretation of 320.392\(A^0\) line in helium as the \((2p^2)^3P^e \rightarrow (1s2p)^3P^0\)-transition by Kruger was later confirmed by Wu on the basis of theoretical calculation. Tech and Ward

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reinvestigated the matter and performed highly accurate spectroscopic measurement of the line $2p^2(3P_e) \rightarrow (1s2p)^3P^0$ at $320.2926 \pm 0.0010\,\text{Å}$. A discrepancy of about $100\,\text{cm}^{-1}$ between the measurements of Tech. et al.\cite{7} and that of Kruger\cite{4} also observed the line $2p^2(3P_e) \rightarrow 1s2p^3P^0$ at $320.40 \pm 0.3\,\text{Å}$. A discrepancy of about $100\,\text{cm}^{-1}$ between the measurements of Tech. et al.\cite{7} and that of Kruger\cite{4} is due to the unavailability of accurate standard wave-lengths at the time of measurement of Kruger\cite{4}. Berry et al.\cite{8} also observed the line $2p^2(3P_e) \rightarrow 1s2p^3P^0$ at $320.40 \pm 0.3\,\text{Å}$. Drake and Dalgarno\cite{9}, Holøien\cite{10}, Bhatia\cite{11} calculated the energy of the $(2p^2)^3P_e$ - state of helium by using variational method. Using variational perturbation method Aashamar\cite{12} obtained the accurate eigenvalue for the $(2p^2)^3P_e$ - state of neutral helium. All these theoretical investigations predicted the wave length of $2p^2(3P_e) \rightarrow 1s2p^3P^0$ transition of helium range from $320.288$ to $320.293\,\text{Å}$, and hence are in agreement with the measurement of Tech. et al.\cite{7}

Under such circumstances it is necessary to perform very accurate spectroscopic calculation of the $(2p^2)^3P_e$ - state of helium. In this article, we propose a method to improve the DES wave function to get not only the best upper bound energy but also rapid convergence with respect to the size of the trial space.

2 Theory

The rotational invariance of the Hamiltonian makes it possible to express the variational equation of two electrons in the field of a fixed nucleus in terms of three independent variables\cite{13}. The three coordinates are the sides of the triangle formed by the three particles i.e., two electrons and the fixed nucleus. The reduction of the three Eulerian angles, defining the orientation of this triangle in space, from the variational equation is an immediate consequence of the spherical symmetry of the field. For any $^3P$ - state of even parity arising from two equivalent electrons, the general variational equation (10) of Ref.\cite{13} reduces to

$$\delta \int \left[ \left( \frac{\partial f^0}{\partial r_1} \right)^2 + \left( \frac{\partial f^0}{\partial r_2} \right)^2 + (r_1^{-2} + r_2^{-2}) \left( \frac{\partial f^0}{\partial \theta_{12}} \right)^2 + (r_1^{-2} + r_2^{-2})(f^0)^2 \frac{1}{\sin^2 \theta_{12}} \right. \\
\left. + 2(V - E)(f^0)^2 \right] dV_{r_1, r_2; \theta_{12}} = 0 \quad (1)$$

subject to the normalization condition

$$\int (f^0)^2 dV_{r_1, r_2; \theta_{12}} = 1 \quad (2)$$

The symbols in equation (1) and (2) are same as of Ref.\cite{13}. We use atomic units throughout.

The correlated wavefunction is given by

$$f^0_1(r_1, r_2, r_{12}) = \eta_1(1)\eta_1(2) \left[ \sum_{l > 0} \sum_{m > 0} \sum_{n \geq 0} B_{lmn} r_1^l r_2^m r_{12}^n \sin \theta_{12} + \text{Exchange} \right] \\
+ \left[ \eta_1(1)\eta_2(2) \sum_{l > 0} \sum_{m > 0} \sum_{n \geq 0} C_{lmn} r_1^l r_2^m r_{12}^n \sin \theta_{12} + \text{Exchange} \right] \\
+ \eta_2(1)\eta_2(2) \left[ \sum_{l > 0} \sum_{m > 0} \sum_{n \geq 0} D_{lmn} r_1^l r_2^m r_{12}^n \sin \theta_{12} + \text{Exchange} \right] \quad (3)$$
where, $\eta \sim e^{-\rho}$ and $\rho$ is the non-linear parameter. The linear coefficients $B$, $C$, $D$ along with energy eigenvalue $E$ are determined by matrix diagonalisation method.

### 3 Results

The results of our calculation are given in Table 1. All calculations were carried out in quadruple precision. The orbital exponents $\rho_1$ and $\rho_2$ were optimized using the Nelder–Mead procedure and are given in Table 1. There are other variational calculations of the $(2p^2)^3P^e$-states for Helium. So far best result was obtained by Bhatia. A comparison of present results to that of Bhatia is given in Table 1. The total number of terms (N) for each calculation is given in the first column. The results obtained by Bhatia in second column are compared with the present results in the last column. It’s remarkable that for a given number of term (N) the results of the present basis sets are better than that of Bhatia for next largest basis set e.g. our result for 21 parameter calculation is better than that of 35 parameter calculation of Bhatia, again our 84 parameter result is better than the 97 parameter result of Bhatia as is evident from Table 1. Substantial reduction of the number of terms i.e. the basis set size is a clear advantage of the present method for a given calculated energy value. It is relevant to mention that using variational-perturbation technique Aashamar obtained the non-relativistic energy for $(2p^2)^3P^e$- state of helium as $0.71050015560a.u.$ Present variational results of $0.710500155678a.u.$ is even slightly lower than that of variational-perturbation results.

Tech et al. observed the sharp line in far ultra-violet region with wave number $312,214.52 \pm 0.97 \text{ cm}^{-1}$ corresponding to a wavelength $320.2926 \pm 0.0010 \text{ A}^0$. In order to compare with experiment, we use the well known experimental line with wave number $169,087.01 \pm 0.15 \text{ cm}^{-1}$ corresponding to the transition $(1s2p)^3P^0 \rightarrow 1s^2(1S)$. Adding the wave number of the above two lines, an experimental value of $481,301.53 \pm 0.98 \text{ cm}^{-1}$ for the energy of the doubly excited $(2p^2)^3P^e$ term relative to the ground $(1s^2)^1S$ results. Similarly, combining the observation of Kruger and the experiment of Martin, an experimental value of $481,205 \text{ cm}^{-1}$ for the energy of the $(2p^2)^3P^e$-term relative to the ground $1s^2(1S)$ results. It is clear that there is a discrepancy of approximately $100 \text{ cm}^{-1}$ between the experimental results of Kruger and Tech. We obtained the position of the $(2p^2)^3P^e$-state above the ground $1s^2(1S_0)$-state by subtracting our calculated energy for the $(2p^2)^3P^e$-state from the well known energy $-637,219.54 \text{ cm}^{-1}$ of the ground $1s^2(1S_0)$ state of helium. The conversion factor $1 \text{ a.u.} = 219,444.528 \text{ cm}^{-1}$ is used. Our calculated value of $481,304.17 \text{ cm}^{-1}$ for the energy of $(2p^2)^3P^e$-state above the ground $(1s^2)^1S_0$-state is far from the experimental value of $481,205 \text{ cm}^{-1}$ of Krugar, but agrees fairly well with the experimental value of $481,301.53 \pm 0.98 \text{ cm}^{-1}$ of Tech et al. Aashamar obtained a value of $481,301.62 \text{ cm}^{-1}$ for the same including mass polarization, relativistic and radiative effects. A difference of approximately $3 \text{ cm}^{-1}$ between our non-relativistic results and that of Aashamar or experiment is due to relativistic and other correction.

Finally taking the difference between the present calculated wave number $481,304.17 \text{ cm}^{-1}$
Table 1: Non-relativistic energy (-E) of He atom in \((2p)^3 P^e\)-state. All energies are in a. u. The non linear parameters are \(\rho_1 = 0.81006481\) and \(\rho_2 = 1.07917071\).

| N  | Bhatia          | PresentMethod          |
|----|----------------|-----------------------|
| 20 | 0.710456705905 |                       |
| 21 | 0.7104996242754|                       |
| 35 | 0.710497876335 |                       |
| 39 | 0.71050006887316|                      |
| 54 | 0.71050014164022|                      |
| 56 | 0.710500049935  |                       |
| 66 | 0.71050014872252|                      |
| 70 | 0.710500140510  |                       |
| 84 | 0.710500142765  | 0.71050015218194      |
| 90 | 0.710500149950  |                       |
| 95 | 0.710500151000  |                       |
| 96 | 0.710500151515  |                       |
| 97 | 0.710500152070  |                       |
| 99 | 0.71050015410607|                       |
| 150| 0.71050015526295|                       |
| 210| 0.71050015554599|                       |
| 267| 0.71050015561803|                       |
| 300| 0.71050015564129|                       |
| 321| 0.71050015564988|                       |
| 336| 0.71050015565678|                       |
for the \((2p^2)^3P^e\)-state above the ground \(1s^2(^1S_0)\)-state of helium and the experimental\(^{15}\) line at wave number 169.087 cm\(^{-1}\) for the transition \(1s2p(^3P^0) \rightarrow 1s^2(^1S_0)\) of helium, we get the wave number 312.217.16 cm\(^{-1}\), corresponding to a wavelength 320.2899\(^0\)\(\AA\) for the transition \(2p^2(^3P^e) \rightarrow 1s2p(^3P^0)\) of helium.

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5 References

1. E. Holøien, Nucl.Instrum. Methods 90, 229(1970)
2. U. Fano, in Atomic Physics, edited by V. W. Hughes, B. Bedeson, V. W. Cohen and F. M. J. Pichanick(Plenum, New York, 1969) p.209
3. K. T. Compton and J. C. Boyce, J. Franklin Inst, 205, 497(1928).
4. P. G. Kruger, Phys. Rev. 36, 855(1930).
5. R. Whiddington and H. Priestley, Proc. Roy. Soc.(London)A 145, 462(1934)
6. T. Y. Wu, Phys. Rev. 66, 291(1944).
7. J. L. Tech and J. F. Ward, Phys. Rev. Lett. 27, 367(1971).
8. H. G. Berry, I. Martinson, L. J. Curtis and L. Lundin, Phys. Rev. A 3, 1934(1971)
9. G. W. F. Drake and A. Dalgarno, Phys. Rev. A 1, 1325 (1970)
10. E. Holoiien, J. Chem. Phys 29, 676(1958); and Phys. Norvegica 1, 53(1960)
11. A. K. Bhatia, Phys. Rev.A. 2, 1667(1970).
12. K. Aashamar, Institute for Theoretical Phys., University of Oslo, Norway, Institute Report No.35,1969
13. Tapan K. Mukherjee and Prasanta K. Mukherjee, Phys. Rev.A 50, 850(1994).
14. J. A. Nelder and R. Mead, Computer J. 7, 308 (1965).
15. W. C. Martin, J. Res. Nat. Bur. Stand. Sect. A 64, 19(1960)