

Variational calculation for the doubly excited state $(2p^2)^3P^e$ of helium

Tapan K. Mukherjee* and Prasanta K. Mukherjee

Department of Spectroscopy, Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700 032, India

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Highly precise variational calculations of nonrelativistic energies of the $(2p^2)^3P^e$ state of the helium atom are presented. We get an upper bound energy $E = -0.7105\ 001\ 556\ 5678$ a.u., the lowest yet obtained.

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I. INTRODUCTION

Multiply excited energy states in atoms have been the subject of many experimental and theoretical investigations. Specially doubly excited states (DES's) for neutral helium is particularly important as the DES's provide a fundamental testing ground of the accuracy of the theoretical treatment. The review article of Holøien [1] and Fano [2] gives a detailed list of references.

A large number of DES's of neutral helium can autoionize to the continuum above the $1s(2S)$ ground state of He^+ . Besides, there are also nonautoionizing doubly excited states in helium. These exactly quantized DES states decay to the lower excited states through electric dipole interaction giving rise to a sharp spectral line. It is worthwhile to mention that relativistically these states may autoionize, but the autoionization lifetimes are still appreciably longer than the mean radiative lifetimes of the allowed electric dipole transition [1].

Compton and Boyce [3], Kruger [4], and Whiddington and Priestley [5] are the pioneers to observe such exactly quantized DES of helium. Among such nonautoionizing doubly excited levels in helium, the $(2p^2)^3P^e$ state is the lowest lying P state of even parity. The interpretation of $320.392\ \text{Å}^0$ line in helium as the $(2p^2)^3P^e \rightarrow (1s2p)^3P^0$ transition by Kruger [4] was later confirmed by Wu [6] on the basis of theoretical calculation. Tech and Ward [7] reinvestigated the matter and performed highly accurate spectroscopic measurement of the line $2p^2(^3P^e) \rightarrow (1s2p)^3P^0$ at $320.2926 \pm 0.0010\ \text{Å}^0$. A discrepancy of about $100\ \text{cm}^{-1}$ between the measurements of Tech and Ward [7] and that of Kruger [4] is due to the unavailability of accurate standard wavelengths at the time of measurement of Kruger [4]. Berry *et al.* [8] also observed the line $2p^2(^3P^e) \rightarrow 1s2p(^3P^0)$ at $320.40 \pm 0.3\ \text{Å}^0$.

Drake and Dalgarno [9], Holøien [10], Bhatia [11] calculated the energy of the $(2p^2)^3P^e$ state of helium by using the variational method. Using the variational perturbation method Aashamar [12] obtained the accurate eigenvalue for the $(2p^2)^3P^e$ state of neutral helium. All these theoretical investigations predicted the wavelength of the $2p^2(^3P^e)$

$\rightarrow 1s2p(^3P^0)$ transition of helium range from 320.288 to $320.293\ \text{Å}^0$, and hence are in agreement with the measurement of Tech and Ward [7].

Under such circumstances it is necessary to perform very accurate spectroscopic calculation of the $(2p^2)^3P^e$ state of helium. In this paper, 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.

II. 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 [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. [13] reduces to

$$\delta \int \left[\left(\frac{\partial f_1^0}{\partial r_1} \right)^2 + \left(\frac{\partial f_1^0}{\partial r_2} \right)^2 + (r_1^{-2} + r_2^{-2}) \left(\frac{\partial f_1^0}{\partial \theta_{12}} \right)^2 + (r_1^{-2} + r_2^{-2}) \times (f_1^0)^2 \frac{1}{\sin^2 \theta_{12}} + 2(V - E)(f_1^0)^2 \right] dV_{r_1, r_2, \theta_{12}} = 0 \quad (1)$$

subject to the normalization condition

$$\int (f_1^0)^2 dV_{r_1, r_2, \theta_{12}} = 1. \quad (2)$$

The symbols in Eqs. (1) and (2) are the same as of Ref. [13]. We use atomic units throughout.

The correlated wave function is given by

*Current address: Department of Physics, Sikkim Manipal Institute of Technology, Majitar, Rangpo, East Sikkim-737132, India.

$$f_1^0(r_1, r_2, r_{12}) = \eta_1(1)\eta_1(2) \left[\sum_{l>0} \sum_{m>0} \sum_{n \geq 0} B_{lmn} r_1^l r_2^m r_{12}^n \sin \theta_{12} + \text{exchange} \right] + \left[\eta_1(1)\eta_2(2) \sum_{l>0} \sum_{m>0} \sum_{n \geq 0} C_{lmn} r_1^l r_2^m r_{12}^n \sin \theta_{12} + \text{exchange} \right] + \eta_2(1)\eta_2(2) \left[\sum_{l>0} \sum_{m>0} \sum_{n \geq 0} D_{lmn} r_1^l r_2^m r_{12}^n \sin \theta_{12} + \text{exchange} \right] \quad (3)$$

where $\eta \sim e^{-\rho r}$ and ρ is the nonlinear parameter. The linear coefficients B , C , D along with energy eigenvalue E are determined by the matrix diagonalization method.

III. RESULTS

The results of our calculation are given in Table I. All calculations were carried out in quadruple precision. The orbital exponents ρ_1 and ρ_2 were optimized using the Nelder–Mead [14] procedure and are given in Table I.

There are other variational calculations [9–11] of the $(2p^2)^3P^e$ states for helium. So far the best result was obtained by Bhatia [11]. A comparison of the present results to that of Bhatia [11] is given in Table I. The total number of terms (N) for each calculation is given in the first column. The results obtained by Bhatia [11] in the second column are compared with the present results in the last column. It is remarkable that for a given number of term (N) the results of the present basis sets are better than that of Bhatia [11] for the next largest basis set, e.g., our result for the 21 parameter calculation is better than that of the 35 parameter calculation of Bhatia [11], again our 84 parameter result is better than the 97 parameter result of Bhatia [11] as is evident from Table I. 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

TABLE I. Nonrelativistic energy ($-E$) of He atom in $(2p^2)^3P^e$ state. All energies are in a.u. The nonlinear parameters are $\rho_1 = 0.810\ 064\ 81$ and $\rho_2 = 1.079\ 170\ 71$.

N	Bhatia	Present method
20	0.710 456 705 905	
21		0.710 499 624 272 54
35	0.710 497 876 335	
39		0.710 500 068 873 16
54		0.710 500 141 640 22
56	0.710 500 049 935	
66		0.710 500 148 722 52
70	0.710 500 140 510	
84	0.710 500 142 765	0.710 500 152 181 94
90	0.710 500 149 950	
95	0.710 500 151 000	
96	0.710 500 151 515	
97	0.710 500 152 070	
99		0.710 500 154 106 07
150		0.710 500 155 262 95
210		0.710 500 155 545 99
267		0.710 500 155 618 03
300		0.710 500 155 641 29
321		0.710 500 155 649 88
336		0.710 500 155 656 78

that using the variational–perturbation technique Aashamar [12] obtained the nonrelativistic energy for the $(2p^2)^3P^e$ state of helium as 0.710 500 155 60 a.u. The present variational results of 0.710 500 155 678 a.u. is even slightly lower than that of variational–perturbation results [12].

Tech and Ward [7] observed the sharp line in the far ultraviolet region with wave number $312\ 214.52 \pm 0.97\ \text{cm}^{-1}$ corresponding to a wavelength of $320.2926 \pm 0.0010\ \text{\AA}$. In order to compare with the experiment, we use the well known experimental [15] 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 [4] and the experiment of Martin [15], 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 [4] and Tech [7]. 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 [7] 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 [4], but agrees fairly well with the experimental value of $481\ 301.53 \pm 0.98\ \text{cm}^{-1}$ of Tech and Ward [7]. 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 nonrelativistic results and that of Aashamar or experiment is due to relativistic and other corrections.

Finally taking the difference between the present calculated wave number $481\ 304.17\ \text{cm}^{-1}$ 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 $169\ 087\ \text{cm}^{-1}$ for the transition $1s2p(^3P^0) \rightarrow 1s^2(^1S_0)$ of helium, we get the wave number $312\ 217.16\ \text{cm}^{-1}$, corresponding to a wavelength $320.2899\ \text{\AA}$ for the transition $2p^2(^3P^e) \rightarrow 1s2p(^3P^0)$ of helium.

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